Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

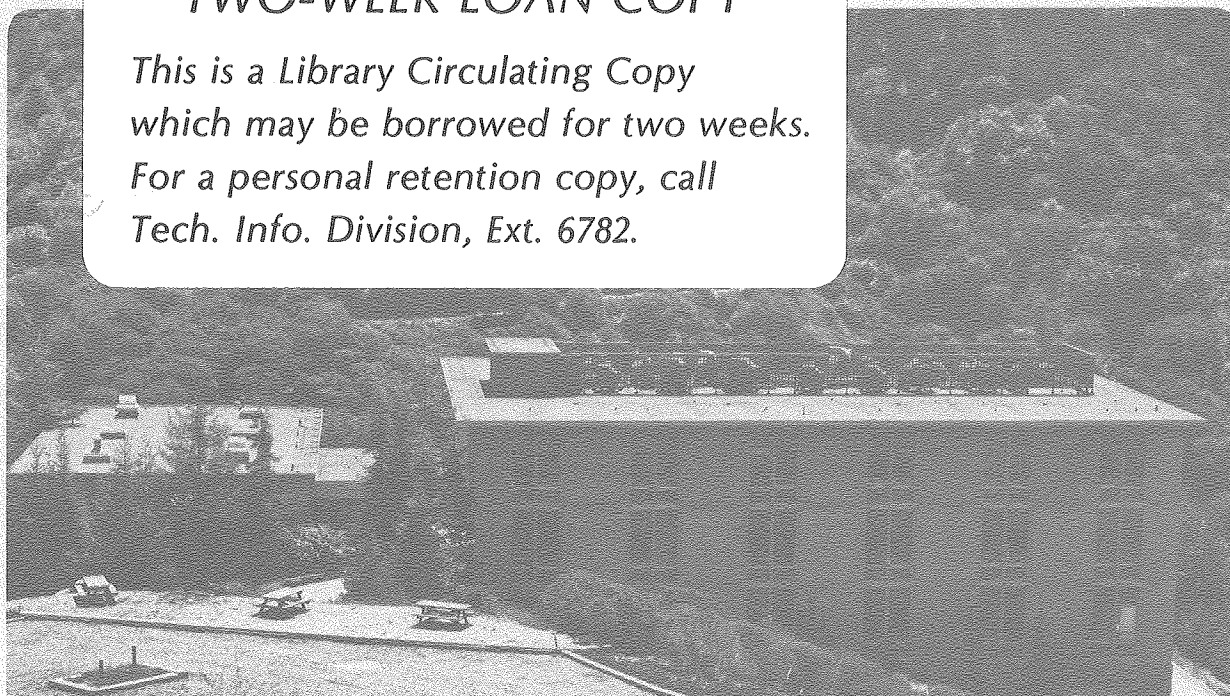HYDROGENATION AND CRACKING OF COAL RELATED FUSED-RING
STRUCTURES USING $ZnCl_2$ AND $AlCl_3$ CATALYSTS

Sadie S. Salim
(Ph.D. thesis)

April 1980

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 6782.*

DISCLAIMER

Hydrogenation and Cracking of Coal Related
Fused-Ring Structures Using ZnCl$_2$ and AlCl$_3$ Catalysts

Sadie S. Salim

Materials and Molecular Research Division, Lawrence Berkeley Laboratory
and Department of Chemical Engineering, University of California
Berkeley, California 94720

April 1980

ABSTRACT

Metal halide catalysts, especially zinc chloride, have been
demonstrated to be effective catalysts for the conversion of coal
to liquid products. Coal is believed to consist of aromatic
structural units joined together by various linkages. The present
work was undertaken to study the effect of zinc chloride and
aluminum chloride on a group of two and three ring aromatic and
hydroaromatic substances representative of those found in coal.
Reactions were carried out in a batch autoclave using cyclohexane
solvent, temperature of 325°C and hydrogen or nitrogen pressure of
1600 psig. Dilute solutions of substrates in cyclohexane and a
catalyst to substrate ratio of 0.54 were used.

Substantial substrate reactivity differences were observed for
reactions in the presence of ZnCl$_2$. Naphthalene slowly hydrogenated
to form tetralin which only cracked to a limited degree to form
alkyl-benzenes. The presence of a hydroxyl group on the 1-position
of a ring in naphthalene greatly enhanced the rate of hydrogenation
to form tetrahydronaphthols with either the ring containing the
hydroxyl group or the neighboring ring saturated. The former
product reacted readily to form tetralin and naphthalene. The
latter cracked forming alkyl-benzenes. The presence of a methyl
group on the 1-position of a ring in naphthalene also enhanced the

rate of hydrogenation of the rings. The enhancing effect of the methyl group was much less pronounced than that of the hydroxyl group. Hydrogenation of anthracene and phenanthrene proceeded more readily than that of naphthalene. Anthracene was much more reactive than phenanthrene. Hydrogenation was followed by cracking of the saturated side rings. No cracking of the central ring was observed for anthracene or phenanthrene, or for fluorene. However, such a process was observed when dihydrobibenzocycloheptene was used as the reactant.

All substrates were quite reactive in the presence of $AlCl_3$. This resulted in substantial tar formation as well as high conversions to liquid products. The differences between the reactivities of the substrates were not as pronounced in this case as those observed in the presence of $ZnCl_2$. Again anthracene was more reactive than phenanthrene which was more reactive than naphthalene. Cracking of the saturated central ring of three-ring compounds occurred for rings containing five and seven carbon atoms, the reactivity towards cracking being higher for the seven carbon ring. Enhancement of reactivity of naphthalene type structures was again observed when methyl or hydroxyl substituents were present.

The source of hydrogen used in hydrogenation and cracking of substrates was found to depend on the nature of the catalyst. In the presence of $ZnCl_2$, gaseous hydrogen was the major source of hydrogen. In the presence of $AlCl_3$, Scholl condensation of substrates or reaction intermediates provided most of the hydrogen.

Reaction networks were proposed for hydrogenation and cracking of substrates based on products of reactions of substrates as well as reactions of products of partial hydrogenation of substrates. These networks were explained in terms of carbonium ion mechanisms.

ACKNOWLEDGMENT

I thank my advisor, Professor Alex Bell, for his guidance, support and patience during this work. I would also like to thank Professor Peter Vollhardt for his help in explaining the reaction mechanisms and other useful suggestions, and Professor Theodore Vermeulen for his helpful comments. This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under contract No. W-7405-Eng-48.

Eugene Power, and his staff in the Electronic Division at Lawrence Berkeley Laboratory, and the staff in the Mechanical Shops of the College of Chemistry and Lawrence Berkeley Laboratory, made important contributions to this work. Dr. Amos Newton deserves special thanks for carrying out the GC/MS analysis.

I appreciate the timely work of Nancy Monroe and Marshal Tuttle, who drew the figures and reaction mechanisms. I am indebted to Nancy Charpentier for her excellent typing of the thesis and her useful comments. She went beyond the call of duty in helping me meet my deadline. I would also like to thank the staff of the Chemcial Engineering Department for lending a helping hand.

I owe many thanks to my family for their continuous moral support during my educational career. Last, but not least, I would like to thank my friends, whose contributions were invaluable; not just to my academic career, but especially to my personal happiness and growth.

TABLE OF CONTENTS

TABLES OF CONTENTS (continued)

LIST OF TABLES

LIST OF TABLES (continued)

LIST OF FIGURES

CHAPTER 1: INTRODUCTION

The shortage of petroleum experienced in recent years has motivated considerable research efforts aimed at producing alternative sources of liquid fuels. One area of particular interest has been the liquefaction of coal. Conversion of coal to a synthetic crude oil is attractive since it could permit the introduction of such a product into a refinery for subsequent upgrading.

Coal is a solid substance with hydrogen to carbon ratio of less than 1.0, with a chemical structure which resembles that of an amorphous hydroaromatic polymer. Conversion of coal to petroleum type products, which have hydrogen to carbon ratios of over 1.5, involves cracking and depolymerization of coal to smaller fragments, addition of hydrogen to terminate these fragments and further addition of hydrogen to the resulting aromatic fragments to produce products more closely resembling petroleum. These structural and chemical modifications can be accomplished by purely thermal processes. However, the use of a catalyst permits the acceleration of the rates of cracking and hydrogenation and offers the opportunity to carry out these processes in a more selective fashion.

In view of these demands, it is highly desirable to learn as much as possible about the mechanisms by which the individual structural elements in coal undergo cracking and hydrogenation. In the present work, a study was undertaken to examine specifically the mechanism and structural dependance of hydrogenation and cracking of a group of two- and three-ring aromatic and hydroaromatic substances representative of those found in structural units of coal. Lewis acid catalysts $ZnCl_2$ and $AlCl_3$ were used for these investigations.

In the remainder of this chapter, some background information for the present investigation is provided. A summary of use of metal halides in coal liquefaction, with emphasis on $ZnCl_2$ and $AlCl_3$, is presented. A description of models for coal structure and the presence and abundance of structures similar to those of the present investigation is given. A summary of the previous studies on hydrocracking reactions of model compounds using metal halide catalysts is presented. Finally, the scope and objectives of the present investigation are discussed.

I. Coal Liquefaction With Metal Halide Catalysts

Lewis acids in the form of metal halides have attracted much attention as coal liquefaction catalysts. These compounds are known to be effective in cracking of carbon-carbon bonds as well as heteroatom removal (1). In the work carried out by Ross et al. a group of metal halide catalysts were rated according to their activity for increasing the solubility of coal in pyridine in the temperature range of 190-210°C (2). Under the reaction conditions used, the order or activity was $AlCl_3 > AlBr_3 \gg SbCl_3 \approx SbF_3 \approx ZnCl_2$.

Aluminum chloride, which is the strongest catalyst of the above group, has been found to be an effective catalyst for coal gasification at severe reaction conditions, 400-500°C and 1500-4000 psig (3). At lower temperatures, ~250°C, coal liquefaction as well as gasification has been observed (3). Aluminum chloride has also been used as a Friedel-Crafts catalyst to alkylate coal and thereby improve its extractability and susceptibility to gasification (4,5). In the work of Ross et al. $AlCl_3$ was found to be very effective in increasing coal solubility in pyridine especially when promoted by HCl (2).

Zinc chloride, which is much less active than $AlCl_3$, is commercially more suitable for coal liquefaction because unlike $AlCl_3$, it is not hydrolyzed in the presence of water and its recovery is much easier than that of $AlCl_3$. Extensive investigations on use of $ZnCl_2$ as a coal liquefaction catalyst have been undertaken. Zinc chloride was used in a pilot plant for coal liquefaction in Japan over thirty years ago (6). Low catalyst concentrations, temperatures above 400°C, and pressures of about 3000 psi hydrogen were used. It was found to be a good catalyst for coal hydrogenation. More recently, extensive work has been undertaken at Conoco Coal Development Co. (formerly Consolidation Coal Co.), by Zielke et al. on developing coal lique- faction processes using $ZnCl_2$ as the catalyst (7,8,9,10). Their processes were based on using approximately equal amounts of catalyst and coal and reaction conditions of 400°C and 3000 psi hydrogen. High yields of gasoline type products were obtained. Investigations were carried out at Montana State University on use of an equimolar mixture of $ZnCl_2$/KCl for coal liquefaction (11). Again high coal conversions were obtained. Use of $ZnCl_2$ for coal liquefaction was also studied at the University of Utah (12,13). Zinc chloride was used directly or impregnated unto the coal, with or without hydrogen gas, under operating conditions of 500°C and 2000 psi hydrogen. Again high coal conversions were obtained. Recent studies at the University of California have been directed toward use of $ZnCl_2$ for hydrocracking of coal or solvent refined coal under relatively mild reaction conditions (14,15,16). When catalyst ratios greater than 1 were used, at temperatures of 200-300°C and pressures below 200 psig hydrogen, high conversions of coal to pyridine soluble materials were obtained (15,16).

II. Coal Structure

Structural studies suggest that coal consists of a network of aromatic clusters joined together by various linkages (17-23). The aromaticity of coal depends on the type of coal studied, the ratio of aromatic to aliphatic carbon increasing with the rank of coal (24-26). A number of models for the structure of coal have been proposed (17-20). According to Wiser's model (18,19), 70-75% of the carbon present in bituminous coal is contained in aromatic structures in form of polycondensed rings. The majority of the rings have six carbons in them, although some five carbon rings are also present. Some rings contain the heteroatoms nitrogen, sulfur or oxygen. Some of the rings are saturated, accounting for 15-25% of the total carbon in coal. In Given's model (17), the polycondensed aromatic rings account for 55-80% of the carbon in bituminous coal. Huston et al. have suggested that 80% of the carbon in the bituminous coal they studied was incorporated into cyclic groups (22). Ten percent of the total carbon in this coal was found to be in saturated rings. Recent measurements of aromaticity by C^{13} NMR have shown that 63% of the carbon in bituminous coal is aromatic (28,29).

The nature and abundance of aromatic units in coal have been investigated in a number of studies. According to Hill and Lyon (20), the number of rings in a cluster may be as high as 5 or 6. Other investigators have suggested that the number of rings in a cluster might be 3 to 6 (30) or 2 to 4 (31). In Given's model (17), the aromatic structure was proposed to be in the form of one, two and three nucleus aromatic clusters, some partially saturated in structures similar to dihydroanthracene. Recent investigations have presented

evidence that a large number of benzene type structures are present in bituminous coal (32). The ratio of two-ring naphthalene type structures to one-ring structures is about 0.25. The ratio of three-ring structures to one-ring structures is about 0.15.

Aliphatic groups are present in coal in the form of side groups as well as bridges between aromatic clusters (20,33). Deno et al. have suggested that C_1, C_2 and higher carbon number bridges as well as side chains are present in coal (34,35). It was previously proposed that most of the alkyl side chains are methyl groups (36). Deno's work also indicates that C_1 groups appear in the form of side chains to aromatic units rather than bridges between units.

The heteroatoms present in coal are nitrogen, sulfur and oxygen. They are present as a part of the ring structure as well as in side groups and bridges (17-23). Oxygen is the most abundant heteroatom, accounting by weight for 10-20% of bituminous coal (23,31,37). The abundance of oxygen decreases with increase in coal rank. The oxygen is present in the form of carboxylic, carbonyl, ether or hydroxyl groups (37). The hydroxyl groups are an important fraction, accounting for 40-60% of the total oxygen (31,37,38).

III. Literature Review

A number of investigations have been carried out on use of metal halides for the hydrogenation and cracking of polycondensed aromatic compounds. A chronological list of the literature pertaining to the reactions of two- and three-ring aromatic compounds in the presence of Lewis acids is given in Table 1-1. The table is subdivided into reactions pertaining to naphthalene, tetralin, methylnaphthalene, naphthol, anthracene, dihydroanthracene, phenanthrene and fluorene, and lists the

Table 1-1

Model Compounds Literature Review

Compound	Catalyst	T, °C	P(H$_2$,psig) at 25°C	P(H$_2$,psig) at T	t, hr		Conversion to Products	Reference
Naphthalene	AlCl$_3$	460	1300–1400		3	60%	to products bliling below 160°C (benzene, toluene, xylenes, etc.) no tar formation	39
Naphthalene	AlCl$_3$	350–490	1200–1500		6-7	–	products included lower boiling liquids, gases, and significant amount of tars	41
Naphthalene	ZnCl$_2$/Al$_2$O$_3$	400	1500		2	86%	to recovered oil, 22% boiling up to 175°C, 36% boiling up to 200°C, benzene, toluene, xylene identified in the products	42
Naphthalene (in isopentane solvent)	TF$_5$/HF	50	500		1	100%	75% to tetralin	44
Naphthalene	ZnCl$_2$	425		3400	1	31.5%	tetralin (17.5%), 1-methylindan (6.4%), alkylbenzens & benzene (5.9%), cycloalkanes (0.6%), hexanes & pentanes (1.2%)	47
Naphthalene	60% ZnCl$_2$ 40% CuCl$_2$	400	1400		3	>98%	alkylnaphthalene & naphthalene & alkyltetralins & tetralin & indans (2.2%), alkylbenzenes & benzenes (46.4%) cycloalkanes (1.5%), C$_5$-C$_7$ alkanes (3.7%), C$_1$-C$_4$ gases (45.7%), coke (0.5%)	53
Tetralin	ZnCl$_2$	425		3400	1	25.9%	1-methylindan (10.3%), alkylbenzenes & benzene (13.4%), cycloalkanes (1.8%) hexanes & pentanes (0.4%)	47

Table 1-1, continued

Compound	Catalyst	T, °C	$P(H_2, psig)$ at 25°C	$P(H_2, psig)$ at T	t, hr	Conversion to Products	Reference
1-Methyl-naphthalene	{60% $ZnCl_2$ {40% CuCl	400	1400		3	>91%	alkylnaphthalenes & naphthalene & alkyltetralins & tetralin & indans (9.8%), alkylbenzenes & benzene (47.7%), cycloalkanes (2.0%), C_5-C_7 alkanes (6.6%), C_1-C_4 gases (33.4%), coke (0.5%)	53
2-Naphthol	$ZnCl_2$	425		3400	1	naphthalene (20.6%), tetralin (43.3%), 1-methyl-indan (8.6%), alkylbenzenes & benzene (21.6%)	47
Anthracene	$FeCl_3$	450	1300-1400		3	36%	to products boiling below 160°C, (High boiling fractions were composed of hydronaphthalenes and hydroanthracenes).	40
Anthracene	$AlCl_3$	355	1500		3	–	products included lower boiling liquids, gases, and significant amount of tars	41
Anthracene	NH_4Cl/Sn	450	3000		10	67%	products included benzene (19.6%), toluene (32.7%), ethylbenzene (14.5%) and lesser amounts of other aromatic hydrocarbons	45
Anthracene	$ZnCl_2$	300		3400	1	81%	nearly all tricyclic compounds (main components dihydro and tetra-hydroanthracenes), 3% bicyclic compounds	46,51
Anthracene	$ZnCl_2$	450		3400	1	99%	partially hydrogenated anthracenes & isomers (11%), bicyclic compounds (9%), monocylic compounds (6%), aliphatic compounds (6%)	46,51

Table 1-1, continued

Compound	Catalyst	T,°C	P(H_2,psig) at 25°C	at T	t,hr		Conversion to Products	Reference
Anthracene	$ZnCl_2$	425		3400	1	93.7%	partially hydrogenated anthracenes (43.6%), alkylnaphthalenes & alkyltetralins & diphenyl-methanes (28.3%), naphthalene (0.8%), tetralin (2.3%), 1-methylindan (0.7%), alkylbenzenes & benzene (10.9%), cycloalkanes (6.8%), hexanes & pentanes (0.3%)	47
Anthracene	$ZnCl_2$ transferred under dry atmosphere	400	1400		1	97.9%	partially hydrogenated anthracenes & isomers (67.2%), alkylnaphthalenes & naphthalene (0.9%), alkyltetralins & tetralin (1.8%), 1-methylindan (1.8%), alkylbenzenes & benzene (3.5%), cyclo-alkanes (3.7%), C_5-C_7 alkanes (0.7%), C_1-C_4 gases (9.6%), high boiling compounds & coke (2.4%)	49
Anthracene	{60% $ZnCl_2$ {40% $CuCl_2$ transferred under dry atmosphere	400	1400		1	99.1%	partially hydrogenated anthracenes & isomers (21.4%), alkylnaphthalenes & naphthalene (2.8%), alkyltetralins & tetralin (27.2%), 1-methyl-indan (6.5%), alkylbenzenes & benzene (10.9%), cycloalkanes (13.1%), C_5-C_7 alkanes (4.8%), C_1-C_4 gases (6.8%), high boiling compounds & coke (5.6%)	49
Anthracene	{60% $ZnCl_2$ {40% $CuCl_2$	400	1400		1	99.8%	partially hydrogenated anthracenes & isomers (12.7%), alkylnaphthalenes & naphthalene (1.6%), alkyltetralins & tetralin (17.3%), 1-methylindan (5.0%), alkylbenzenes & benzene (12.7%), cycloalkanes (16.9%), C_5-C_7 alkanes (8.6%), C_1-C_4 gases (15.8%), high boiling compounds & coke (9.2%)	49
Anthracene	{80% $ZnCl_2$ {20% $CuCl_2$ transferred under dry atmosphere	400	1400		1	99%	partially hydrogenated anthracenes & isomers (24.1%), alkylnaphthalenes & naphthalene (2.1%), alkyltetralins & tetralin (19.3%), 1-methylindan (5.6%), alkylbenzenes & benzene (9.9%), cyclo-alkanes (13.7%), C_5-C_7 alkanes (4.8%), C_1-C_4 gases (13.4%), high boiling compounds & coke (6.1%)	49

8

Table 1-1, continued

Compound	Catalyst	T,°C	P(H$_2$,psig) at 25°C	at T	t,hr		Conversion to Products	Reference
Anthracene	80% ZnCl$_2$ 20% CuCl	400	1400		1	99%	partially hydrogenated anthracenes & isomers (16.0), alkylnaphthalenes & naphthalene (3.4%), alkyltetralins & tetralin (14.5%), 1-methylindan (6.9%), alkylbenzenes & benzene (13.2%), cyclo-alkanes (10.5%), C$_5$-C$_7$ alkanes (6.2%), C$_1$-C$_4$ gases (23.5%) high boiling compounds & coke (4.8%)	49
Anthracene	80% CuCl 20% KCl	400	1400		1	96.1%	partially hydrogenated anthracenes & isomers (75.3%), alkylnaphthalenes & naphthalene (0.3%), alkyltetralins & tetralin (2.4%), alkylbenzenes & benzene (0.3%), cycloalkanes (0.1%), C$_1$-C$_4$ gases (11.5%), high boiling compounds & coke (6.2%)	49
Anthracene	ZnCl$_2$	400		3400	2	100%	to partially hydrogenated anthracenes & isomers, bicyclic compounds, monocyclic compounds & aliphatic compounds	51
Anthracene	60% ZnCl$_2$ 40% CuCl	400	1400		3	>98%	anthracene & partially hydrogenated anthracenes & isomers (2.5%), alkylnaphthalenes & naphthalene & alkyltetralins & tetralin & indans (8.9%), alkyl-benzenes & benzene (27.7%), cycloalkanes (10.8%), C$_5$-C$_7$ alkanes (7.9%), C$_1$-C$_4$ gases (38.1%), coke (4.1%)	53
Anthracene	SnCl$_3$	125	Ar atm		1.5	57%	dihydroanthracene (24%), tetrahydroanthracene (3%), bianthracenes & other products (30%)	54
9,10-Dihydro-Anthracene	60% ZnCl$_2$ 40% CuCl	400	1400		3	>98%	anthracene & partially hydrogenated anthracenes & isomers (2.4%), alkylnaphthalenes & naphthalene & alkyltetralins & tetralin & indans (9.1%), alkyl-benzenes & benzene (29.5%), cycloalkanes (8.6%), C$_5$-C$_7$ alkanes (7.2%), C$_1$-C$_4$ gases (42.0%), coke (1.2%)	53

6

Table 1-1, continued

Compound	Catalyst	T,°C	P(H_2,psig) at 25°C	at T	t,hr		Conversion to Products	Reference
Phenanthrene	AlCl$_3$	355	1200		4	–	products included lower boiling liquids, gases, and significant amount of tars	41
Phenanthrene	{60% ZnCl$_2$ 40% CuCl$_2$	400	1400		1	75.1%	partially hydrogenated phenanthrenes & isomers (44.6%), alkylnaphthalenes & naphthalene (0.6%), alkyltetralins & tetralin & indans (10.9%), alkylbenzenes & benzene (3.3%), cycloalkanes (2.2%), C$_5$-C$_7$ alkanes (0.3%), C$_1$-C$_4$ gases (3.2%), high boiling compounds and coke (9.7%)	52
Phenanthrene	ZnCl$_2$	400	1400		3	12.5%	partially hydrogenated phenanthrenes & isomers (11.5%), alkylnaphthalenes & naphthalene (0.4%), alkyltetralins & tetralin & indans (0.1%), alkylbenzenes and benzene (0.1%)	52
Phenanthrene	{60% ZnCl$_2$ 40% CuCl$_2$	400	1400		3	98.6%	partially hydrogenated phenanthrenes & isomers (3.0%), alkylnaphthalenes & naphthalene (2.2%), alkyltetralins & tetralin & indans (12.4%), alkylbenzenes & benzene (33.2%), cycloalkanes (7.0%), C$_5$-C$_7$ alkanes (7.2%), C$_1$-C$_4$ gases (27.7%), high boiling compounds & coke (5.9%)	52
Phenanthrene	{80% ZnCl$_2$ 20% KI	400	1400		3	36.6%	partially hydrogenated phenanthrenes & isomers (33.1%), alkylnaphthalenes & naphthalene (0.1%), alkyltetralins & tetralin & indans (2.2%), cycloalkanes (0.1%), C$_1$-C$_4$ gases (0. %)	52
Phenanthrene	{90% ZnCl$_2$ 10% NiCl$_2$	400	1400		3	66.6%	partially hydrogenated phenanthrenes & isomers (21.5%), alkylnaphthalenes & naphthalene (1.0%), alkyltetralins & tetralin & indans (10.5%), alkylbenzenes & benzene (10.5%), cycloalkanes (7.5%), C$_5$-C$_7$ alkanes (1.4%), C$_1$-C$_4$ gases (11.2%), high boiling compounds & coke (2.0%)	52

Table 1-1, continued

Compound	Catalyst	T, °C	P(H_2), psig at 25°C	at T	t, hr		Conversion to Products	Reference
Phenanthrene	$ZnCl_2$	400	1400		1	44.5%	partially hydrogenated phenanthrenes (37.7% alkylnaphthalenes & naphthalene (0.4%), alkyltetralins & tetralin & indans (0.9%), alkylbenzenes & benzene (0.3%), C_1-C_4 gases (1.6%), high boiling compounds & coke (3.6%)	52
Fluorene	$AlCl_3$	25	N_2 atm		2	52%	polymerization to bifluorenyl	43
Fluorene	60% $ZnCl_2$ 40% CuCl	400	1400		3	>82%	biphenyls (14.3%), alkylbenzenes & benzene (25%), cycloalkanes (6.5%), C_5-C_7 alkanes (4.2%), C_1-C_4 gases (30.6%), coke (1.9%)	53
Fluorene (in chloro-benzene solvent)	66% $AlCl_3$ 33% CuCl	25	N_2 atm		2	25-71%	conversion to bifluorenyl	55

reaction conditions and product yields for each compound.

The earliest studies reported are those of Kling and Florentin (39,40). These investigators used small quantities of $AlCl_3$ and $FeCl_3$ to crack naphthalene and anthracene at relatively severe reaction conditions. Winter et al. also used low concentrations of $AlCl_3$ and $FeCl_3$ and severe reaction conditions for hydrocracking of naphthalene, anthracene and phenanthrene (41). They reported high conversions, mostly to gaseous and tarry products. Schmerling proposed the use of $ZnCl_2$, impregnated on Al_2O_3, and severe reaction conditions to hydrogenate and crack aromatic hydrocarbons (42). Siskin and Wristers used a variety of metal halides, each together with its corresponding protonic acid to hydrogenate fused ring aromatics (44). The reactions were carried out in an aliphatic solvent using high catalyst concentrations and mild reaction conditions. Blom et al. used a metal together with NH_4Cl to hydrogenate and crack anthracene (45). Both hydrogenation and cracking of the substrates were observed.

In recent years, Morita, Kikkawa, Nakatsuji and their coworkers have carried out a number of experiments on use of metal halides for hydrogenation and cracking of a number of polycondensed aromatic compounds (46-53). They used large amounts of a metal halide, or a mixture of metal halides and high temperatures and pressures. High conversions to products were observed. Gas formation was observed in most cases, sometimes accounting for up to 40% of the total conversion. The highest conversions were obtained using a catalyst mixture of 60% $ZnCl_2$ and 40% CuCl (49,53). The above investigators proposed that the hydrogenolysis reaction of fused ring aromatic compounds proceeds through a multistage mechanism involving hydrogenation, isomerization and hydrocracking.

Three-ring compounds are thus converted to two-ring compounds which in turn are converted to alkylbenzenes.

Other investigations include the work of Poutsma et al. on the polymerization of anthracene (54) and the work of Prey (43) and Wen (55) on the polymerization of fluorene. These experiments were carried out under mild reaction conditions and dimers of the initial substrates were the major products. Polymerization of anthracene provided the hydrogen necessary for its hydrogenation to dihydroanthracene and tetrahydroanthracene (54).

IV. Purpose and Scope of the Present Investigation

The manner in which catalysts, in particular metal halides, promote the reaction of specific structural elements of coal is not well understood. The present investigation was undertaken to provide information about the behavior of some of the structural units of coal in the presence of metal halide catalysts.

In the process of hydrogenolysis of coal, the bonds joining the aromatic clusters may be broken. It is also possible to hydrogenate and crack the rings in each cluster. The substituent groups on a ring may be removed in the hydrocracking process. These groups may also effect the hydrogenation and cracking of that ring or the neighboring rings.
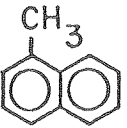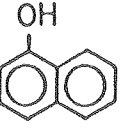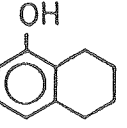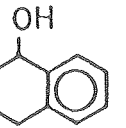
In the present study, the hydrogenation and cracking of aromatic clusters and the effect of substituent groups on this process were investigated. This was accomplished by studying the reactions of a series of fused ring aromatic model compounds under mild reaction conditions. A mild Lewis acid, $ZnCl_2$, and a strong Lewis acid, $AlCl_3$ were used as catalysts.

A list of the model compounds used in this study is presented in Table 1-2. The compounds include unsaturated two-ring aromatic clusters, some with methyl or hydroxyl substituent groups, and hydro-aromatic compounds resulting from the partial hydrogenation of the two-ring aromatic compounds. Three-ring compounds in Table 1-2 include anthracene, phenanthrene and products resulting from their partial hydrogenation. Compounds having 5 or 7 carbons in their central ring were also investigated. While the reactions of most of these compounds have been investigated previously, these studies were conducted at high pressures and temperatures with the result that only the final reaction products could be observed in most cases. As a consequence it was not possible to establish clearly the reaction sequences linking initial reactants to intermediate and final products. To overcome these limitations, dilute concentrations of the substrates in an inert solvent were utilized in this work in conjunction with temperatures and hydrogen pressures which in most instances would allow only partial conversions of the reactants. More clearly stated, the objectives of the present investigation were:

1. To obtain information about the relative reactivities of each structure in the presence of $ZnCl_2$ and $AlCl_3$,

2. To study the effect of acid strength and reaction conditions on hydrogenation and cracking of each structure,

3. To identify the source of hydrogen used in hydrogenation and cracking of the compounds investigated in the presence of the above catalysts, and,

4. To propose possible reaction mechanisms for hydrogenation and cracking of two and three-ring aromatic clusters in the presence of metal halide catalysts.
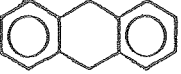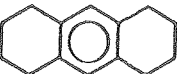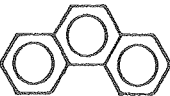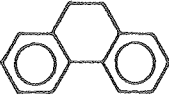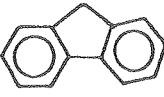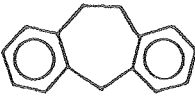
Table 1-2

Model Compounds

Substrate	Molecular Structure
Naphthalene	
1,2-Dihydronaphthalene	
Tetralin	
1-Methylnaphthalene	
1-Naphthol	
5,6,7,8-Tetrahydro-1-naphthol	
1,2,3,4-Tetrahydro-1-naphthol	

Table 1-2, continued

Substrate	Molecular Structure
Anthracene	
9,10-Dihydroanthracene	
1,2,3,4,5,6,7,8-Octahydroanthracene	
Phenanthrene	
9,10-Dihydrophenanthrene	
Fluorene	
9,10-Dihydro-5H-Dibeno [a,d]-cycloheptene	

CHAPTER 2: EXPERIMENTAL

I. The Autoclave and Related Parts

The experiments were carried out in one of two autoclaves. For operational safety, each autoclave was situated in an explosion-proof bay. These bays were constructed from 1/2 inch steel plates with sliding steel doors, and were equipped with blow out roofs. The main control panel for control and monitoring of the reactions in the autoclaves was located outside the explosion proof bays. The gas feed system, including gas cylinders and a booster pump, was also located outside the bays.

Most of the experiments were carried out in autoclave system #1. A schematic diagram of this system is presented in Fig. 2-1. Autoclave system #2 was similar to system #1, but excluded the injector and gas sampling parts. The autoclave and related equipment were supported by a steel table which was bolted to the floor of the reaction bay.

A. The Autoclave

The autoclave was constructed of 316 stainless steel (Autoclave Engineers, Inc., Model APB-300). It was rated for operational conditions of up to 5000 psig at 350°C. The internal volume of the autoclave system was 300 cm^3. In the present experiments, a glass liner was used to facilitate the introduction and removal of the reaction components. Thus, the working volume of the autoclave was reduced to 280 cm^3.

The body of the autoclave contained three ports for gas introduction and removal. Gases could be introduced into the autoclave through the injector by means of valves 1a, 1b and 1d or directly through valves 1a and 1c. One of the outlet ports lead to pressure monitoring equipment, gas sampling equipment and vent valves. The other
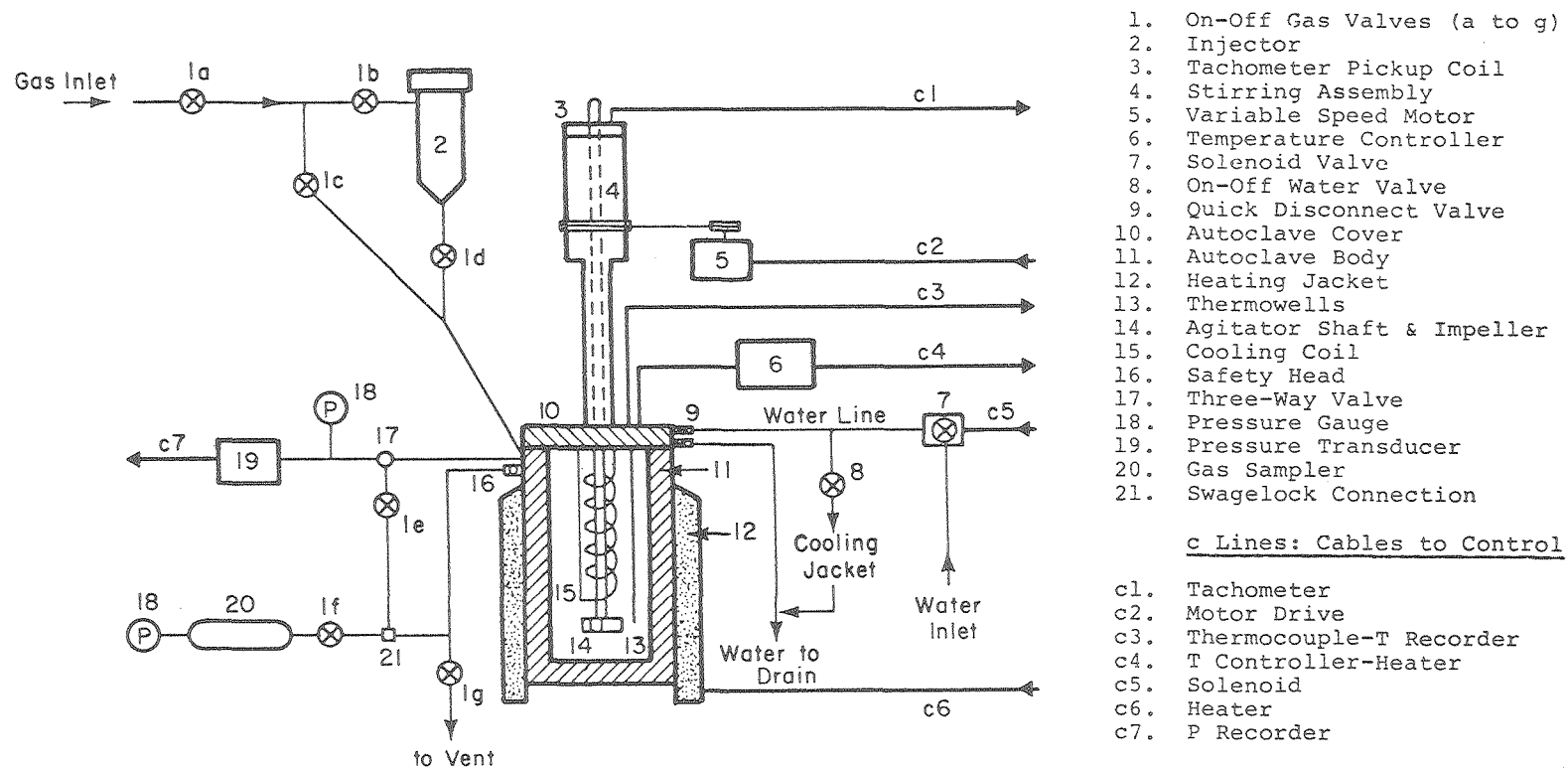
Fig. 2-1. Experimental Apparatus

1. On-Off Gas Valves (a to g)
2. Injector
3. Tachometer Pickup Coil
4. Stirring Assembly
5. Variable Speed Motor
6. Temperature Controller
7. Solenoid Valve
8. On-Off Water Valve
9. Quick Disconnect Valve
10. Autoclave Cover
11. Autoclave Body
12. Heating Jacket
13. Thermowells
14. Agitator Shaft & Impeller
15. Cooling Coil
16. Safety Head
17. Three-Way Valve
18. Pressure Gauge
19. Pressure Transducer
20. Gas Sampler
21. Swagelock Connection

c Lines: Cables to Control

c1. Tachometer
c2. Motor Drive
c3. Thermocouple-T Recorder
c4. T Controller-Heater
c5. Solenoid
c6. Heater
c7. P Recorder

XBL 803-8915

which also lead to the vent line, contained a safety assembly. This assembly consisted of a teflon coated Inconel rupture disc, which was rated at 5394 psig at 72°F and 5016 psig at 400°F.

The cover of the autoclave was a circular flange which made a seal with the body of the autoclave by means of a stainless steel gasket. Six hexagonal screws tigthened the flange to the autoclave body. The cover had a circular opening in the center for the stirring assembly.

B. The Stirring Assembly

Stirring of the autoclave contents was accomplished by a rotating propeller. The propeller was attached to a shaft which was magnetically coupled to external rotating magnets. Rotation was provided by a variable speed DC motor (1/4 hp, maximum 2500 rpm). The variable speed control and AC/DC convertor for this motor were located on the main control panel. A stator coil, which was fitted over the top of the magnetic drive assembly, acted as a pick up coil for a tachometer. The tachometer was also located on the main control panel. The stirring shaft made a seal at the central opening of the autoclave cover. This seal was made between a knife edge seating in the shaft and a thin stainless steel gasket placed inside the autoclave cover.

C. The Injector

The injector was designed to introduce liquid samples into the autoclave. It was built from a solid rod of 316 stainless steel. The structure and dimensions of the injector are given in Fig. 2-2. The side arm of the injector was made by welding a standard 1/4 in OD, 316 stainless steel tube to the body. A Viton "O" ring, 0.862 ID, 1.068 OD, was housed inside the groove on the top of the injector body. The cover of the injector was silver plated to prevent it from galling to the
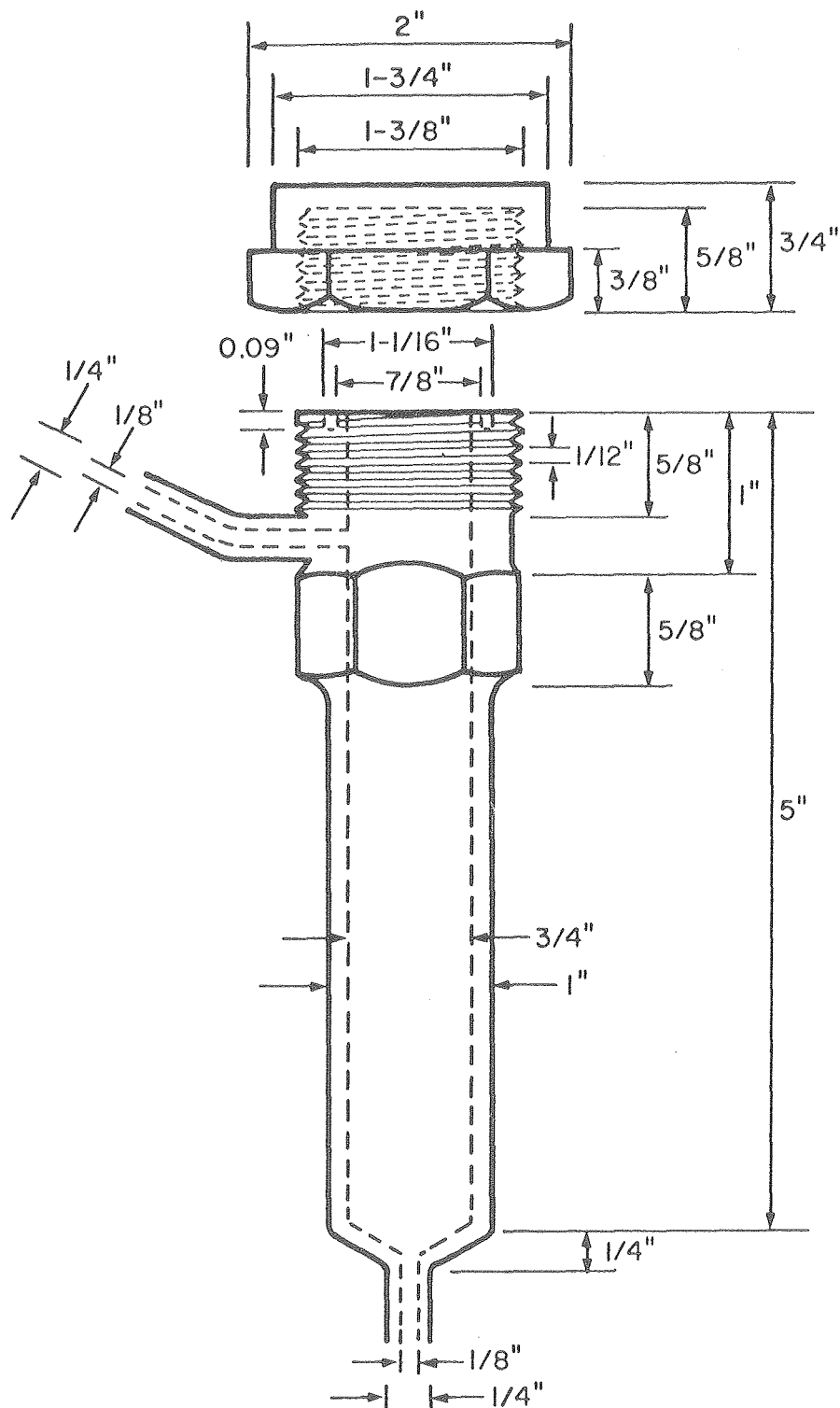
Fig. 2-2. The Injector

XBL 803-8913

injector body. Hexagonal cuts were made on the cover and the body of
the injector. This was done to make it possible to use wrenches for
tightening the cover onto the body. However, with the present design
and use of the Viton "O" ring, hand tightening was sufficient to pro-
vide a suitable seal. The injector and corresponding valves were
pressure tested at room temperature up to 4000 psig. With this design,
the contents of the injector could be transferred into the autoclave in
a fraction of a second with a pressure difference of 50 psig.

D. The Heating System

The heating of the autoclave was accomplished by a 1200 watt
heating mantle (Autoclave Engineers, Model VF-8500). The heater was
supported on the table in such a manner that it could be removed at the
end of each experiment to facilitate cooling of the system. Power to
the heater was provided by a temperature controller (Honeywell Dial
Trol R7350 A&G). The temperature signal to the controller came
directly from an iron-constantan thermocouple situated in one of the
two thermowells. The signal from the temperature controller to the
heating mantle, went through the main control panel located outside the
bay. Thus, it was possible to turn off the heater at any time from
outside the reaction bay. The other thermowell contained a copper-
constantan thermocouple. This thermocouple lead directly to the
temperature recorder located on the main control panel.

The controller provided the desired reaction temperature within a
range of $\pm$ 5°C for temperatures up to 225°C. Better control was
obtained at higher temperatures. At 325°C, the control range was
within $\pm$ 2°C. The heat-up times for experiments at 225°C and 325°C
are presented in Table 2-1.

Table 2-1

Autoclave Heat up and Cool down Times

	experiments at T = 225 ± 4°C			experiments at T = 325 ± 2°C	
	T,°C	t,min		T,°C	t,min
Heat up	25	0		25	0
	150	12		150	12
	225	19	Heat up	225	16
				325	26
				325	0
	225	0		225	1
	150*	1	Cool down	150*	8
Cool down	100	2		100	9
	25	12		25	20

* Cooling jacket put in place

E. The Cooling System

The autoclave and its contents were cooled by means of an internal cooling coil as well as an external cooling jacket. The flow of water through the 1/8 in. stainless steel cooling coil cooled the autoclave cover as well as contents. A solenoid valve actuated the flow of water to the main water line. The on-off control switch for the solenoid valve was located on the main control panel. A water valve, which was placed in line to the cooling coil, redirected the flow of water to the cooling jacket as desired. The cool down times for experiments at 225°C and 325°C are presented in Table 2-1.

F. The Gas Feed System

The autoclave could be pressurized with hydrogen or nitrogen either directly from the gas cylinders or through a booster pump. The gas tanks, the pump and necessary valves were located outside the reaction bay. The main inlet valve, valve 1 in Fig. 2-1, was located inside the bay. The gas lines were each fitted with check valves to prevent back filling of the cylinders. A line filter was placed in the joint nitrogen-hydrogen gas line to trap out particulate matter. This line lead to a valve which directed the gases to the booster pump or the reaction bay.

The booster pump was a pneumatically driven diaphram pump (American Instrument Co., Model 46-14025). It was possible to pressurize the contents of the autoclave up to 5000 psig using this pump.

The gas pressure inside the autoclave could be monitored by a standard dial gauge. The line attached to the gauge was also connected to a pressure transducer (Teledyne Taber, Model 2801) which transmitted a signal to the recorder on the main control panel.

G. The Gas Collecting System

When it was desired to collect a gas sample, the gas collecting

system was placed in line by a swagelock connection. As shown in

Fig. 2-1, this system consisted of a gas collecting cylinder, a

pressure gauge and a valve. The gas collector was made of 304 stainless

steel (Matheson, 4HD75, double connection). It had a volume of 75 ml

and a pressure rating of 1800 psig. The pressure gauge measured

pressures of 0-200 psig.

H. The Cable Junctions

As indicated in Fig. 2-1, seven electrical lines labeled c1-c7,

connected the equipment inside the reaction bay to the control panel

outside. The layout of the cable connections for systems #1 and #2

is presented in Fig. 2-3. For system #1, the electrical wires from DC

motor to motor drive (c2), stator coil to tachometer (c1) and transducer

to pressure recorder (c7) lead to cable junction 1B. The wires from

temperature controller to heater (c4), power to heater (c6) and the

signal to solenoid valve (c5) lead to cable junction 1C. Cables 1B and

1C, originating from junction boxes 1B and 1C, left the reaction bay

through an opening in the wall. They were connected to cable junction

1A inside the main control panel. The copper-constantan thermocouple

wire left the room independantly through the same wall opening and was

connected to the thermocouple junction on the main control panel. The

layout was similar for system #2, with cables B and C leaving the room

and being connected to cable junction A. The thermocouple wire of

system #2 also lead directly to the thermocouple junction. Each of the

cable junction boxes 1B, 1C, B and C had 5 available plugs. Only three

of these plugs were taken by the available wires in each box. This left

25
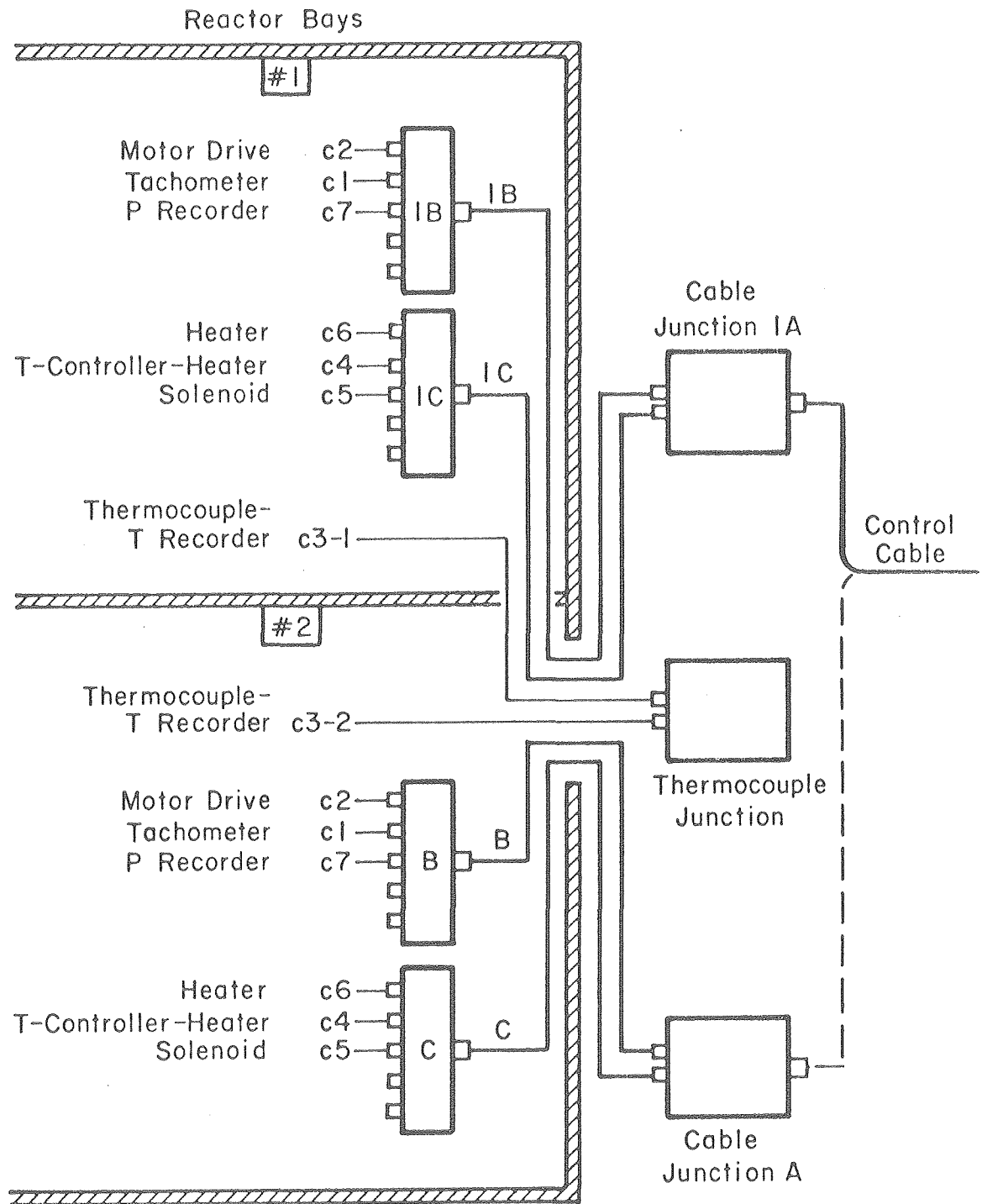
Fig. 2-3. Cable Junctions

XBL 803-8911

two open plugs in each box, four in each system, for possible future additions to each system.

I. The Control Panel

A front view of the control panel is given in Fig. 2-4. Cables 1B and 1C were plugged into cable junction 1A, in back of the front panel. Cables B and C were plugged into cable junction A, also in back of the front panel. The control cable could be plugged into either cable junction A or 1A, depending on which autoclave was to be used. The thermocouple junction switch was also set, depending on which autoclave was to be used, to direct the proper signal to the temperature recorder. A Leeds and Northrup Speedomax recorder type G was used with a temperature range of 0-350°C. A Leeds and Northrup Speedomax recorder type G was also used to record pressure. This recorder displayed the voltage provided by the current signal from the transducer, after passing through the variable resistor in the pressure transducer control box.

During the operation of the autoclave, the same heating and cooling controls and the same pressure and temperature recorders were used for both autoclaves. Thus, by selecting the appropriate thermocouple, pressure transducer control and motor drive control, it was possible to operate one autoclave at a time.

The control system was designed in such a manner that by addition of a temperature and a pressure recorder, a duplicate of the heater and solenoid control box and another control cable, both autoclave systems could be operated simultaneously. Provisions were also made for utilizing additional cables originating from junction boxes 1B, 1C, B and C.
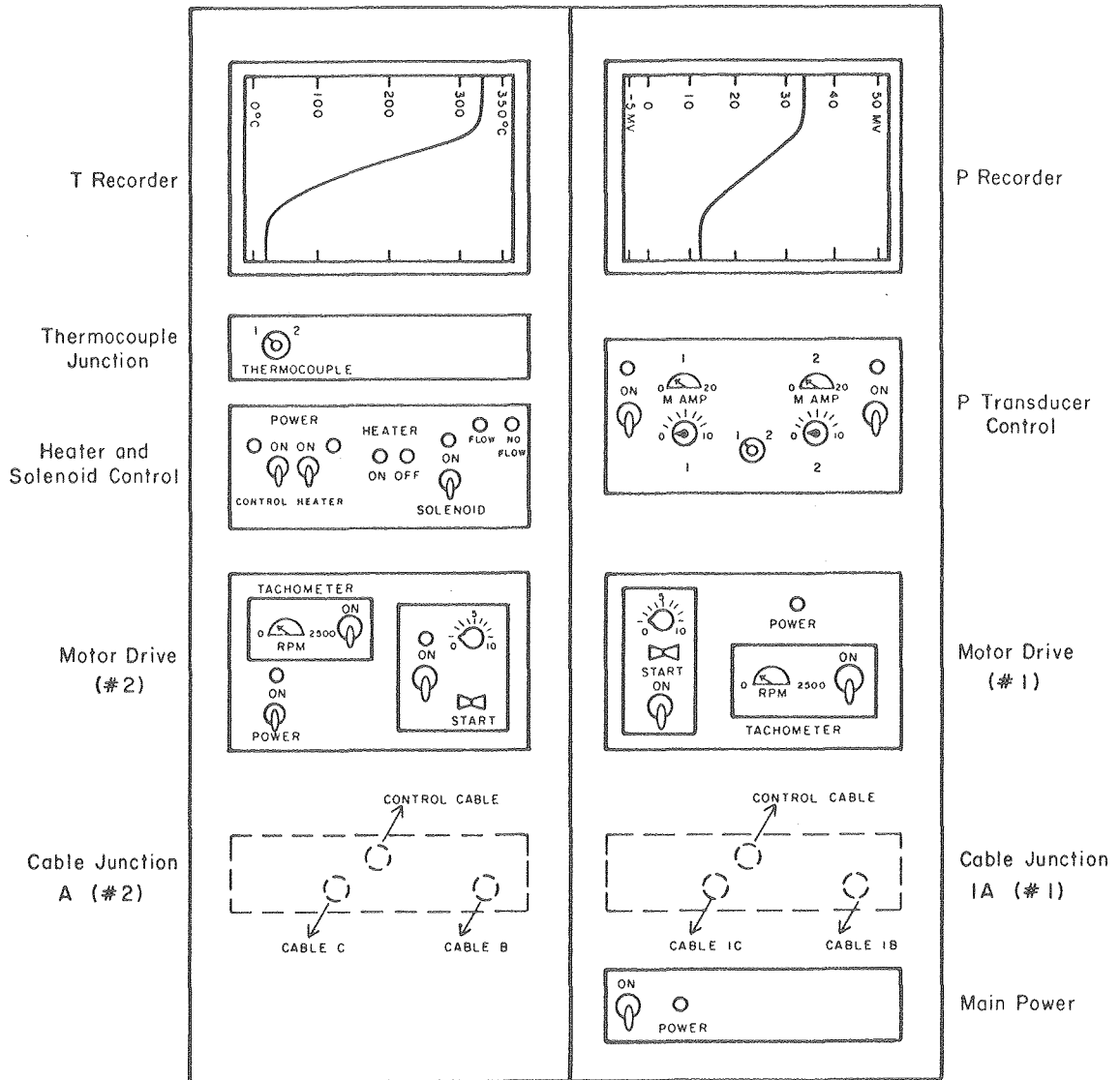
Fig. 2-4. The Control Panel

XBL 803-8914

Table 2-3

Catalysts, Solvents, and Additives

	Compound	Source	Purity or Grade	M.P. [*] (°C)	B.P. [*] (°C)
I.	Catalyst				
	Aluminum Chloride	Mallinkrodt, Inc.	Reagent	190/2.5 atm	sub. 177.8
	Zinc Chloride	Mallinkrodt, Inc.	Reagent	283	732
II.	Solvent				
	Cyclohexane	Matheson, Colleman & Bell	Spectroquality	6.5	80.7
	n-Hexane	Aldrich Chem. Co.	Spectrophotometric	-95	68-69
	n-Decane	Matheson, Colleman & Bell	Reagent	-29.7	173-175
	Benzene	Mallinkrodt, Inc.	Analytical Reagent	5.3	80.1
	p-Xylene	Matheson, Colleman & Bell	Reagent	12-13	138.3
III.	Additive				
	Pyridine	Mallinkrodt, Inc.	Analytical Reagent	-42	115.3
	Sodium Hydroxide	Mallinkrodt, Inc.	Analytical Reagent	318.4	1390

[*]Data obtained from manufacturers' information or Handbook of Chemistry & Physics, 59th ed., ed. by R. C. Weast, CRC Press, Inc., West Palm Beach, Florida (1979).

Table 2-4

Substrates

Substrates	Chemical Structure	Source	Purity or Grade	M.P.[*] (°C)	B.P.[*] (°C)
Naphthalene		Matheson, Colleman & Bell	Reagent	80-81	218
1,2-Dihydronaphthalene		Aldrich Chem. Co.	Technical	-8	89/16 mm
Tetralin		Baker	99+%	-35.8	207
1-Methylnaphthalene		Aldrich Chem. Co.	97%	-22	240-243
1-Naphthol		Aldrich Chem. Co.	99+%	95-96	278-280 (sub. 288)
5,6,7,8-Tetrahydro-1-Naphthol		Aldrich Chem. Co.	99%	69-71	464-365/705 mm
1,2,3,4-Tetrahydro-1-Naphthol		Aldrich Chem. Co.	97%		102-104/2 mm
Anthracene		Eastman	Reagent	216-218	340
9,10-Dihydroanthracene		Aldrich Chem. Co.	98%	108-110	312
1,2,3,4,5,6,7,8-Octahydroanthracene		Pfaltz & Bauer, Inc.	Reagent	78	293-295
Phenanthrene		Eastman	Reagent	99-101	340
9,10-Dihydrophenanthrene		Aldrich Chem. Co.	97%	32-35	168-169/15 mm
Fluorene		Aldrich Chem. Co.	98%	112-115	298
10,11-Dihydro-5H-dibenzo-[a,d]cycloheptene		Aldrich Chem. Co.	98%	74-76	164-165/2 mm

[*]Data obtained from the manufacturers' information or Handbook of Chemistry & Physics, 59th ed., ed. by R. C. Weast, CRC Press Inc., West Palm Beach, Florida (1979)

the catalyst. Then, if necessary, an appropriate amount of the additive was added to the liner. The liner and its contents were placed inside the autoclave. Two to four 0.01 in thick strips of stainless steel, 1/8 in x 5-1/2 in, were wedged between the glass liner and the interior of the autoclave. This was to prevent the liner from spinning during the operation of the autoclave. The cover of the autoclave was tightened to the body. The system was flushed with the appropriate gas, hydrogen or nitrogen, a few times and leak tested. Then it was filled with the proper amount of the gas to give the desired pressure at reaction temperature.

The proper connections were made on the control panel, depending on which autoclave system was to be used. The magnetic stirrer speed was set at 500 rpm. For reactions at 325°C and above, the temperature controller was set at the desired reaction temperature. This resulted in less than 5°C temperature overshoot. The temperature returned to the desired value in a few minutes and stayed within a range of $\pm$ 2°C. For experiments at 225°C, the temperature controller was initially set at 160°C. There was a 70°C overshoot. When a temperature of 230°C was reached, the controller was set at 225°C. This gave a temperature range of 225 $\pm$ 4°C. For experiments at other temperatures, initial control settings were selected to give less than 5°C overshoot with respect to the desired temperature. The heat up times for experiments at 225°C and 325°C are given in Table 2-1.

Once the reaction mixture was at the desired temperature, the experiment was carried out for the desired length of time (60 min in most cases). At the end of this time, the heating mantle was removed. The connections from the water lines to the autoclave cover were made.

The solenoid valve was switched on to open the flow of water through the cooling coil. When the temperature of the contents of the autoclave was reduced to 150°C, the cooling jacket was raised to immerse the auto-clave. The water valve for the flow of water through the cooling jacket was opened. This procedure was undertaken to prevent breakage of the glass liner by thermal shock. The cool down times for the autoclave are given in Table 2-1.

In most of the preliminary experiments, the cooling jacket was not used. For these experiments, cooling from 150°C to room temperature (25°C) took 90 min. Most of this time was required for cooling the contents below 100°C. Rapid cooling was achieved in the substrate reactivity experiments and diagnostic experiments using the cooling jacket and the procedure outlined above.

Two experiments were carried out with naphthalene as substrate, a solvent and $AlCl_3$ as catalyst using the injector. In these experiments half of the solvent and all the catalyst were loaded into the glass liner. The substrate was dissolved in the other half of the solvent and loaded into the injector. The injector and the autoclave were flushed separately with the gas. The autoclave was pressurized to an initial pressure which would result in a final pressure 500 psig below the desired reaction pressure. The autoclave was then heated up to 225°C by setting the temperature controller at 160°C. The injector was pressurized to 100 psig above the autoclave pressure. By opening the valve under the injector, the contents were quickly transferred into the autoclave. Immediately after injection of the cold solvent, the temperature of the autoclave contents dropped 40°C, but returned to 225°C in 3 min. The temperature controller was then set at 225°C and

the pressure adjusted to the desired value. The experiments were
carried out for one hour at 225°C. Since the solvent was in contact
with the AlCl₃ catalyst during the heat up time, considerable solvent
reaction took place before injection of the substrate. This interfered
substantially with product analysis. Therefore, the injector was not
used in any more experiments.

Gas samples were collected after the mixture was cooled. The gas
sampler was flushed three to four times with the gaseous contents of
the autoclave. Then it was filled to a pressure of 200 psig. The auto-
clave pressure was then brought down to atmospheric pressure, the system
was flushed with nitrogen and taken apart. The glass liner was removed.
Ten to twenty percent of the contents remaining in the autoclave was
transferred back to the liner.

C. Cleaning the Autoclave

After each reaction, the autoclave was washed with soap and water,
rinsed with water and acetone and dried. The autoclave was then
partially filled with acetone. The system was flushed with nitrogen,
then pressurized to 50 psig. It was heated to 200°C and kept at that
temperature for 30 min. In this manner, the lines to the autoclave were
cleaned. After cooling the autoclave and removing the acetone, the
autoclave was again washed with soap and water and rinsed with water
and acetone. The stirring assembly was taken apart and rinsed with
water and acetone. The system was left to dry until the next experiment.

III. Product Analysis

The liquid-solid mixture recovered in the glass liner was filtered
through a Whatman #41 filter paper. The resulting liquid was analyzed.
The gases collected in the gas sampler were also analyzed. The solids

collected on the filter paper and remaining in the glass liner were dried and weighed.

A. Gas Analysis

The gas samples were analyzed for methane, ethane, ethylene, propane and propylene. These analyses were carried out only to obtain an approximation to the extent of gasification of the substrates. A Varian Associates, Model 1420 gas chromatograph, equipped with a thermal conductivity detector was used for the analysis. Gases were introduced into the GC through a 1 cm^3 sample loop. A Poropak Q column, 124 cm long, 0.48 cm OD was used. The chromatograph was operated with a carrier gas (He) flow rate of 60 cm^3/min, column temperature of 125°C, detector temperature 140°C and TC detector filament current of 250 mA.

A Matheson certified standard gas mixture was used to calibrate the peak heights. The mole fraction of each component i was calculated from the corresponding peak height according to equation 2-1:

$$(\text{mole fraction})_i = (\text{peak height x attenuation})_i \times \left(\frac{\text{mole fraction}}{\text{peak height x attenuation}}\right)_{\text{standard}} \qquad (2-1)$$

Since the concentrations of gases in hydrogen were low, the conversions were approximated from equation 2-2:

$$(\text{conversion})_i = 100 \times (\text{mole fraction})_i \times \frac{\text{mole } H_2}{\text{mole substrate}} \qquad (2-2)$$

The moles of hydrogen inside the autoclave were calculated from the initial reaction conditions and the ideal gas law.

There was no substrate gasification in experiments in the presence of $ZnCl_2$. In the experiments in the presence of AlC_3, gasification of substrates was in the order of a few percent or less. Since this value

was low and uncertain, it was omitted from the calculations. (See

Chapter 3, section III). The moles of hydrogen inside the autoclave

were calculated from the initial reaction conditions and the ideal gas

law.

B. Liquid Analysis

The liquid samples were analyzed by gas chromatography. Some of

the liquid samples were also analyzed by gas chromatography-mass

spectrometry to identify unknown peaks and confirm the GC identification

of the known peaks.

The gas chromatograph used was a dual column GC (Varian Associates,

Model 1420-10), equipped with linear temperature programming and a

thermal conductivity detector. The columns were 10 ft long, 1/8 in OD,

packed with 5% OV-225 on Chromosorb P support. Helium was used as the

carrier gas at a flow rate of 30 ml/min. The chromatograph was operated

with an injector temperature of 250°C, a detector oven temperature of

280°C and a detector filament current of 150 mA. A column temperature

of 80°C was used to identify and separate compounds lighter than cyclo-

hexane. For complete analysis of each sample, the columns were pro-

grammed for temperature of 80 + 15 °C/min up to 240°C and holding at

240°C for 10-15 min. The recorder (Linear Instruments Corp.) used in

connection with the GC was equipped with an integrator to give a linear

representation of the peak areas.

The elution times for different compounds were obtained using

standard solutions of each compound in cyclohexane. Table 2-5 presents

an average value for the times with respect to cyclohexane. These are

times measured from the maximum point of the cyclohexane peak to that of

each compound.

Table 2-5

Elution Times and Correction Factors with Respect to Cyclohexane

Compound	Chemical Structure	t_i, min	F_i
Butanes	C_4H_{10}	−0.50	0.90
Pentanes	C_5H_{12}	−0.40	0.90
Hexanes	C_6H_{14}	−0.25	0.90
Methylcyclopentane		−0.11	0.90
Cyclohexane		0.0	1.0
Cyclohexane		0.0	1.0
Methylcylohexane		0.25	0.90
Benzene		0.55	0.80
Ethylcyclohexane		0.80	0.90
Toluene		1.20	0.81
Ethylbenzene		1.95	0.82
p-Xylene		2.05	0.82
Hydrindan		2.2	0.83
o-Xylene		2.35	0.82
Propylbenzene		2.70	0.83
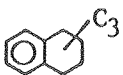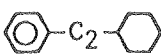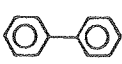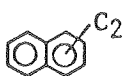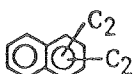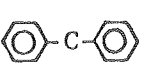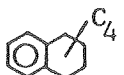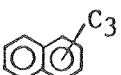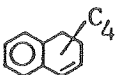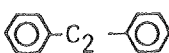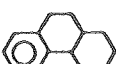
Table 2-5, continued

Compound	Chemical Structure	t_i, min	F_i
Cis- and trans-decalins		2.80 & 3.40	0.88
Methylethylbenzene		2.85	0.83
Trimethylbenzene		2.90	0.83
Propenylbenzene		3.70	0.83
iso-Butylbenzene		3.80	0.83
o-Diethylbenzene		3.88	0.85
Indan		4.0	0.85
Methylindans		4.30 & 4.85	0.86
Indene		4.65	0.85
Methylpropenylbenzene		4.95	0.85
Tetralin		5.40	0.88
Dihydronaphthalene		5.90	0.88
Naphthalene		6.70	0.88
1-Methyltetralin		6.30	0.88
5-Methyltetralin		7.0	0.88
Dimethyl or ethyltetralin		7.4	0.88
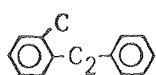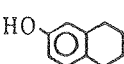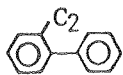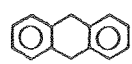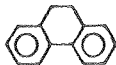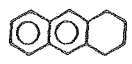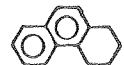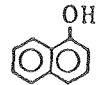
Table 2-5, continued

Compound	Chemical Structure	t_i, min	F_i
1,2,3,4-Tetrahydro-1-naphthol		7.45	0.95
1-Methylnaphthalene		7.8	0.89
1-Decalone		7.9	0.95
2-Methylnaphthalene		8.1	0.89
Propyltetralin		8.2	0.88
Phenylcyclohexylethane		8.3	0.90
Biphenyl		8.4	0.90
Ethylnaphthalene		8.4	0.89
Diethylnaphthalene		8.5	0.89
Diphenylmethane		8.6	0.90
Butyltetralin		8.75	0.89
Propylnaphthalene		9.2	0.89
Butyldihydronaphthalene		9.3	0.89
Bibenzyl		9.3	0.90
Asym— octahydroanthracene		9.4	0.92
Asym — octahydrophenanthrene		9.4	0.92
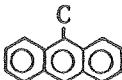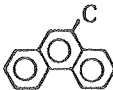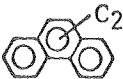
Table 2-5, continued

Compound	Chemical Structure	t_i, min	F_i
1-Tetralone		9.6	0.95
Butylnaphthalene		9.7	0.90
2-Methylbibenzyl		9.85	0.93
Sym— octahydroanthracene		10.2	0.93
Sym— octahydrophenanthrene		10.8	0.93
Fluorene		10.85	0.93
5,6,7,8-Tetrahydro-1-naphthol		10.9	0.95
5,6,7,8-Tetrahydro-2-naphthol		11.6	0.95
2-Ethylbiphenyl		11.7	0.93
Dihydroanthracene		11.9	0.95
Dihydrophenanthrene		11.9	0.95
Tetrahydroanthracene		12.6	0.95
Tetrahydrophenanthrene		12.6	0.95
10,11-Dihydro-5H-dibenzo-[a,d]cycloheptene		13.4	0.94
1-Naphthol		14.2	0.95

Table 2-5, continued

Compound	Chemical Structure	t_i, min	F_i
Anthracene		15.3	0.95
Phenanthrene		15.3	0.95
2-Naphthol	HO	15.5	0.95
Methylanthracene	C	18.1	0.95
Methylphenanthrene	C	18.1	0.95
Dimethylanthracene	C_2	19.5	0.95
Dimethylphenanthrene	C_2	19.5	0.95

Two examples of the gas chromatograms of the liquid products of the experiments are given in Fig. 2-5 and Fig. 2-6. A list of the compounds corresponding to the peak numbers in Fig. 2-6 is given in Table 2-6. The reaction products of experiments with $ZnCl_2$ catalyst were easily identifiable, as can be seen in Fig. 2-5. But for experiments using $AlCl_3$ catalyst, the identifications were much more difficult, due to overlapping peaks. This can be seen in Fig. 2-6. In such cases, a mixture of the standard solution of the compound corresponding to each peak and the sample were injected into the GC for peak identification.

The GC-MS used in this study was a Finnigan Instrument Model 4023 system. It was comprised of a Finnigan Model 9610 gas chromatograph with a flame ionization detector, a Finnigan Model 4000 quadripole mass spectrometer and a Model 2400 Finnigan/Incos data system. The chromatograph contained a glass column, 2 m long, 2 mm ID, packed with 3% OV225 on Chromosorb W/HP. The operation conditions were helium glas flow rate of 20 ml/min, injector temperature of 240°C, and column oven temperature of 70 + 10°C/min up to 200°C and holding at 200°C for 15-20 min. A complete mass spectrum was taken every three seconds.

The mass spectrum of each GC peak was compared to the cracking patterns for known compounds stored in the memory of the computer. A dimensionless number in the range of 0-1000 was generated which indicated the quality of the fit between a peak and a known compound. A value over 800 was considered to indicate a good fit.

The GC-MS output of run #116 (Fig. 2-6) is presented in Fig. 2-7. The compounds corresponding to the scan numbers and the corresponding fits are given in Table 2-6 together with the data for Fig. 2-6. In cases where the peaks overlapped to a great extent, it was not possible to identify the peaks by the GC-MS method.
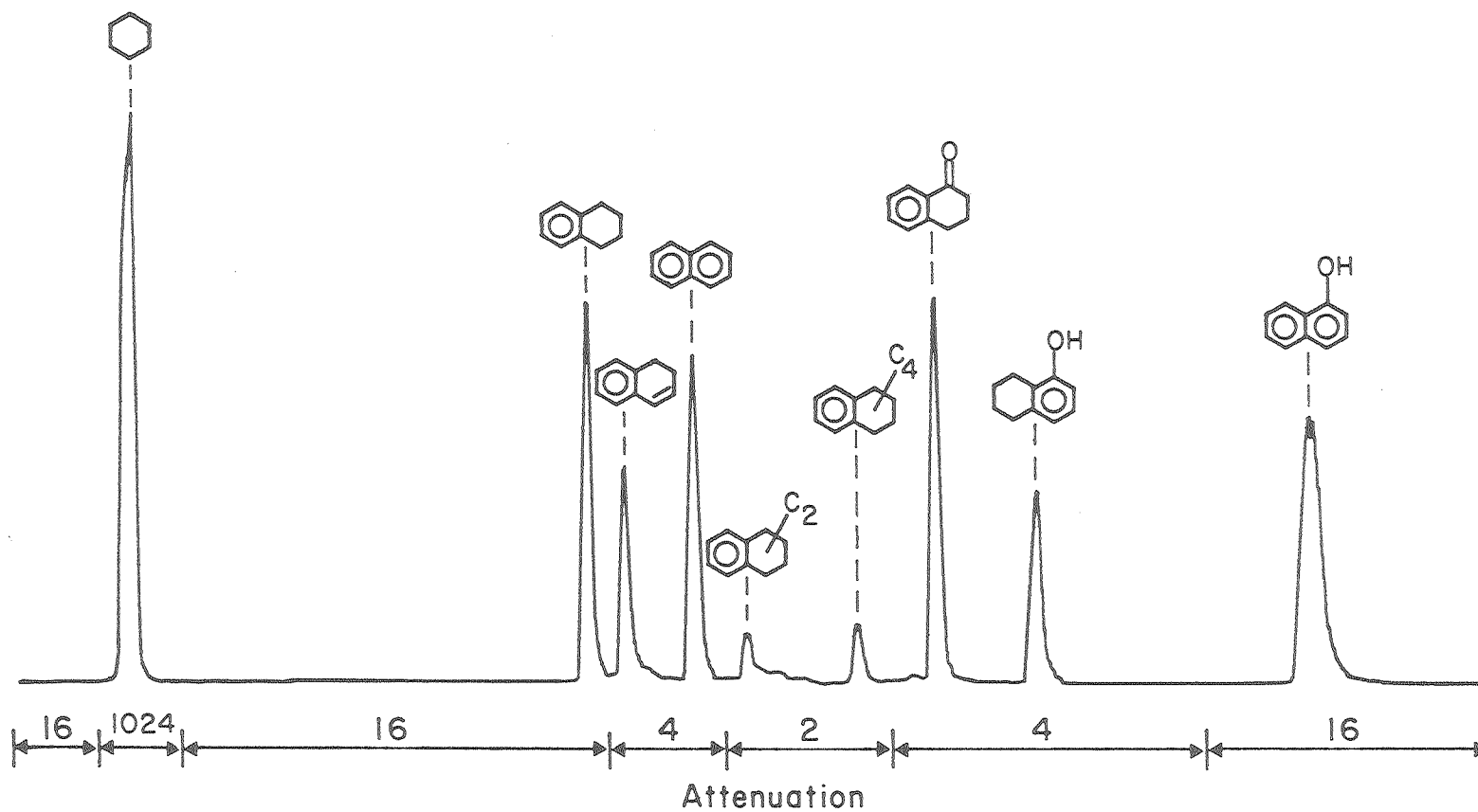
Fig. 2-5. Gas Chromatograph of Liquid Reaction Products of Run # 143
Solvent= Cyclohexane, Substrate= 1-Naphthol, Catalyst=
$ZnCl_2$, T= 325 °C, P= 1600 psig

Fig. 2-6. Gas Chromatograph of Liquid Reaction Products of Run # 116
Solvent= Cyclohexane, Substrate= Dihydrophenanthrene,
Catalyst= AlCl$_3$, T= 325 °C, P= 1600 psig
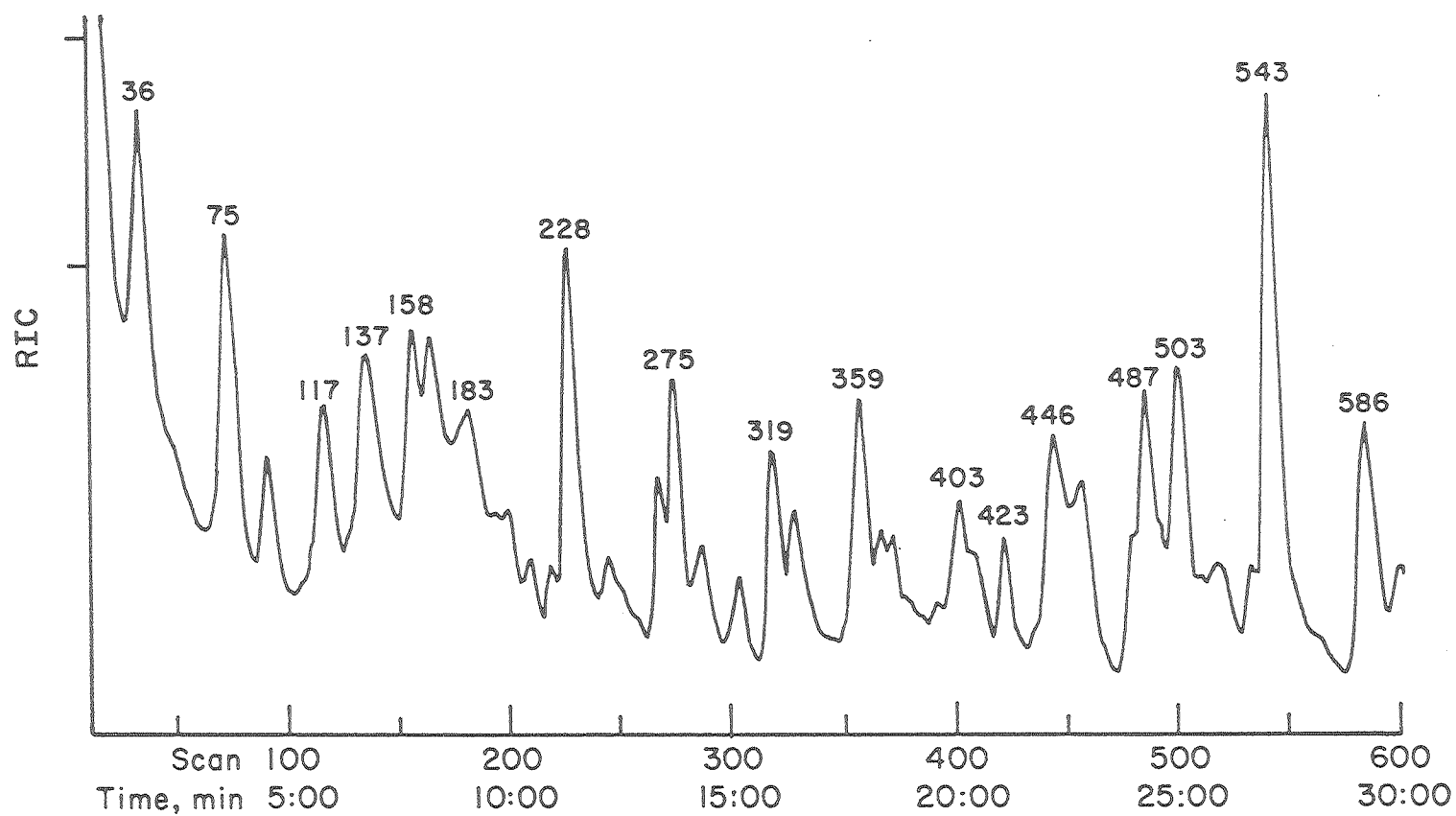
XBL 803-8909

XBL 803-8910

Fig. 2-7. GC/MS Output of Liquid Reaction Products of Run # 116
Solvent= Cyclohexane, Substrate= Dihydrophenanthrene,
Catalyst= AlCl$_3$, T= 325 °C, P= 1600 psig

Table 2-6

Compounds According to Peak # and Scan # with GC-MS Fit

Peak # (Fig. 2-6)	Scan # (Fig. 2-7)	Compound	Chemical Structure	Fit
1		Alkanes	$C_4H_{10}-C_6H_{14}$	
2		Cyclohexane		
3		Benzene		
4		Ethylcyclohexane	C_2	
5	36	Toluene	C	950
6	75	Ethylbenzene	C_2	900
7	92	o-Xylene	C C	890
8	117	Methylethylbenzene or Trimethylbenzene	C C_2 or C C C	850
9 10	137	Butylbenzenes	C_4	
11	158	Diethylbenzene	C_2 C_2	
12	166	Indan		
13	183	Methylindan	C	810
14	201	Indene		
15	210	Methylpropenylbenzene	C C_3	780
16	219	Methylindan	C	810
17	228	Tetralin		870
18	246	Dihydronaphthalene		
19	268	1-Methyltetralin	C	800
20	275	Naphthalene		920
21	287	5-Methyltetralin	C	810

Table 2-6, continued

Peak # (Fig. 2-6)	Scan # (Fig. 2-7)	Compound	Chemical Structure	Fit
22	304	Ethyltetralin		810
23	319	1-Methylnaphthalene		860
24	329	2-Methylnaphthalene		680
25	359	Ethylnaphthalene		
26	367	Dimethylnaphthalene		860
27	373	Butyltetralin		840
28	403	Butyldihydronaphthalene		780
29	423	Butylnaphthalene		920
30	446	Sym. octahydroanthracene		870
31	459	Sym. octahydrophenanthrene		
32	480	2-Ethylbiphenyl		830
33	487	Dihydrophenanthrene		920
34	503	Tetrahydrophenanthrene		
35	543	Phenanthrene		930

After all the peaks were identified by GC and GC-MS techniques, the concentration of the products and the conversion of the substrate to each product were determined from the GC output. Three standard solutions of each compound i in cyclohexane in a concentration range close to that of the sample were prepared. A weight correction factor, F_i, for each compound was defined as:

$$F_i = \frac{W_i/W_c}{A_i/A_c} \qquad (2-4)$$

where

W_i = weight of compound i in solution

W_c = weight of cyclohexane in solution

A_i = peak area of compound i in the GC output

A_c = peak area of cyclohexane in the GC output

An average value of F_i with a precision of 1-3% was obtained for each compound. For some compounds standards were not easily obtainable, or solubility limitations interfered with obtaining F_i using the above procedure. In such cases, a value for F_i was approximated based on that of isomers or similar compounds. A list of the weight correction factors is given in Table 2-5.

The weight concentration of each compound in the product mixture, C_i, was calculated from equation 2-5:

$$C_i = \frac{F_i \times \dfrac{A_i}{A_c}}{\Sigma F_i \times \dfrac{A_i}{A_c}} \qquad (2-5)$$

Where A_i and A_c are peak areas of compound i and cyclohexane in the sample solution.

The percent molar conversion of the substrate to each product, X_i, was calculated from equation 2-6:

$$X_i = C_i \times \frac{L}{R_t} \times \frac{1}{(MW)_i} \times \frac{1}{m_s} \qquad (2\text{-}6)$$

Where:

L = weight of liquid recovered in the product

R_t = total recovery (including solids)

m_s = initial moles of substrate

$(MW)_i$ = molecular weight of compound i

C. Solid Analysis

There was no tar formation in the experiments with $ZnCl_2$ catalyst. In a few cases precipitation or polymerization of the substrate was noticed. Substantial tar formation was observed in the experiments with $AlCl_3$ catalyst. No attempt was made to identify the products in tar. When there was no substrate precipitation, the weight of tar was calculated from the difference between the total solid recovered and the initial catalyst loading. A value for weight% conversion of reactants to tar was obtained from the ratio of weight of tar to the initial weight of substrate plus solvent. This value was only an indication of the extent of tar formation, since tar formation also took place inside the stirring assembly and gas lines.

In cases where there was no solvent interference in the reactions, conversion of the substrate to tar was calculated from equation 2-7:

$$\text{conversion to tar} = 100 - \sum_i X_i \qquad (2\text{-}7)$$

The number obtained here included higher molecular weight compounds which were soluble in cyclohexane as well as tar.

CHAPTER 3: RESULTS AND DISCUSSION

As discussed in the introduction, the experiments have been divided into four groups: 1 - Preliminary experiments, 2 - Substrate reactivity experiments in the presence of $ZnCl_2$, 3 - Substrate reactivity experiments in the presence of $AlCl_3$ and 4 - Diagnostic experiments. The experiments will be discussed in this chapter in the above order. The present chapter also includes a section on reaction mechanisms. This section is based on the results of the experiments presented in the first four sections.

The following convention is used in presenting the results in tables in this chapter beginning with Table 3-4. First a list of wt% concentration of liquid reaction products is presented in the order of their relative elution times from the gas chromatograph. The only exceptions are tetrahydroanthracene/tetrahydrophenanthrene, which are presented before, instead of after, dihydroanthracene/dihydrophenanthrene. In some cases, partial or complete overlapping of GC peaks interfered with identification or calculation of exact concentration of each product. In such cases, compounds are grouped together and a sum concentration value is reported in the table. For experiments in the presence of $AlCl_3$ catalyst, following the above values, wt% conversion of reactants (substrate plus solvent) to tar is reported. The final section of the tables contains a list of mole% conversion of substrates to products. In this list, sums of conversion of substrates to groups of products are reported to simplify and summarize the results. This section of the tables is used most frequently for comparison and explaining the results. The last two values appearing in tables for experiments in the presence of $AlCl_3$ are defined in section I-B of this chapter.

I. The Preliminary Experiments

These experiments were carried out to help select the following reaction conditions for subsequent experiments: 1 - solvent, 2 - reaction time, 3 - substrate concentration, 4 - catalyst to substrate ratio, 5 - reaction temperature and 6 - hydrogen pressure. Most of the experiments were carried out using naphthalene and $AlCl_3$. The experimental procedure for these experiments is given in Chapter 2, section II-B.

A. Solvent Selection

A solvent was used in the present studies to dilute the substrate and to facilitate product recovery and analysis. To minimize the interference of solvent-related reactions with the chemistry of the dissolved substrates, it was necessary to identify solvents which were relatively inert in the presence of $ZnCl_2$ and $AlCl_3$.

A number of aromatic and aliphatic solvents with naphthalene solubilities of about 20 wt% were selected for screening. It should be noted that the less soluble substrates such as anthracene or naphthol were only soluble to the extent of a few percent at room temperature in these solvents. The reactivity of each solvent was first studied at room temperature. Aluminum chloride was added to each solvent with or without naphthalene. Each mixture was stirred, then stored at room temperature and pressure for a few days. The reaction conditions and results of these experiments are presented in Table 3-1. Benzene and xylene polymerized at room temperature in the presence of $AlCl_3$. Cracking of decane was observed. Hydrogenation of naphthalene to tetralin was observed in all cases. The conversion was 70% using benzene as the solvent, 0.3% using cyclohexane and negligible using decane.

Table 3-1

Reactions of Solvents and Naphthalene at Room Temperature

and Pressure Using $AlCl_3$

Solvent	Mole% Naphthalene	Mole% $AlCl_3$	t, Days	Observation	Conversion of Naphthalene to Tetralin, mole%
Benzene	-	5	4	tar	-
Benzene	10	5	4	tar	70
p-Xylene	-	7	2	much tar	-
p-Xylene	6	6	2	much tar	not measured
Cyclohexane	-	3	2	solvent isomerization, 0.1%	-
Cyclohexane	6	2	2	tar	0.3
n-Decane	-	11	1	solvent cracking, 1%	-
n-Decane	17	5	1	tar	trace

These results indicated that xylene and decane were not suitable
solvents due to high polymerization of the former and cracking of the
latter. High conversion of naphthalene in benzene and the tar formation
observed in the reaction of benzene indicated that Scholl condensation
of benzene took place even at room temperature in the presence of AlCl$_3$
catalyst.

$$2 \bigcirc \xrightarrow[-2H]{AlCl_3} \bigcirc\!\!-\!\!\bigcirc \qquad etc.$$

biphenyl
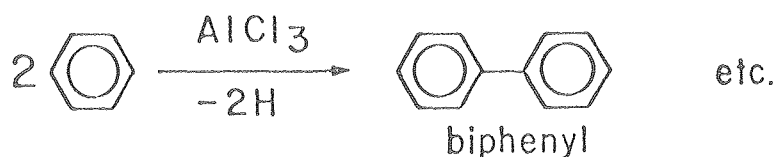
The hydrogen released in the condensation of benzene, hydrogenated
naphthalene to form tetralin. Similar results have been observed under
more severe reaction conditions (56). Conversion of naphthalene to
tetralin was also observed in cyclohexane solvent, although to a much
lower extent. This may be explained by the Scholl condensation of
naphthalene itself to release the hydrogen required for hydrogenation
(57).

$$2 \; \bigcirc\!\!\bigcirc \xrightarrow[-2H]{AlCl_3} \quad \xrightarrow[-2H]{AlCl_3} \quad etc.$$

binaphthyl   perylene
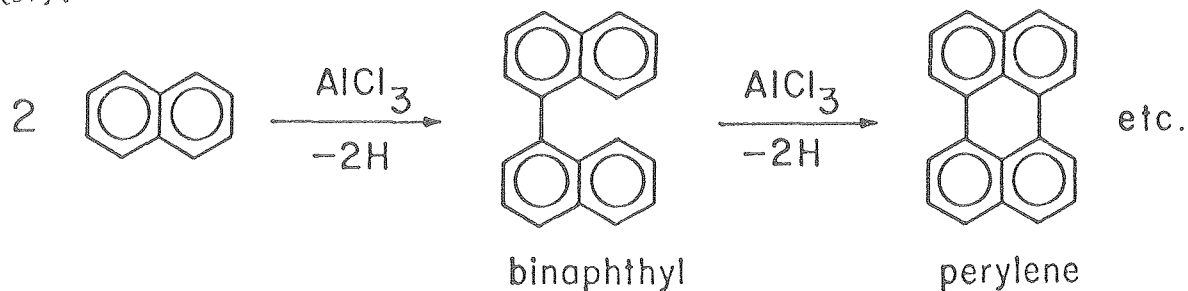
The next group of experiments were carried out in the autoclave
using each of the solvents benzene, cyclohexane, decane, n-hexane and
AlCl$_3$ catalyst. The experimental conditions and results are presented
in Table 3-2. There was evidence of cracking of straight chain
aliphatic solvents and isomerization, dehydrogenation and cracking of

Table 3-2

Reactions of Solvents Using AlCl$_3$ Catalyst

Reaction Conditions: T = 220-240°C, P(H$_2$, at 25°C) = 850-1000 psig, P (at T) = 1400-1800 psig, t = 1 hr at T

Run#	Solvent	Mole% AlCl$_3$	wt% Conversion to Products		
			Tar	Liquid Products	Gases
1	Benzene	0.65	1.0	alkanes 0.03, cyclohexane 0.006, toluene 0.06, ethylbenzene 0.18, xylenes 0.013, biphenyl 0.06	–
3	Cyclohexane	0.82	~0	alkanes 0.8, methylcyclopentane 50.0, methylcyclohexane 0.3, benzene 0.3, ethylcyclohexane 0.08, propylcyclohexane 0.08, toluene 0.04, propylbenzene etc. 0.8	–
4	n-Decane	1.30	0.1	cracked products 2.0	~5
6	n-Hexane	1.10	0.01	cracked products 1.0, higher alkanes 2.0	~5

cyclohexane. Similar results have been obtained in the presence of AlCl$_3$ under a variety of reaction conditions (58-61). Polymerization, hydrogenation and cracking of benzene occurred, as has been observed previously (56,59). Two experiments were carried out using naphthalene with either benzene or cyclohexane solvents and AlCl$_3$ catalyst. The reaction conditions and results are presented in Table 3-3. The solvents were not as reactive when the substrate was present. The conversion of cyclohexane to methylcyclopentane was reduced from 50% to 1% in the presence of naphthalene. Total naphthalene conversion and tar formation in either solvent were approximately the same, although higher conversion to hydrogenated products was observed when benzene was used as the solvent.

Considering the high conversion of naphthalene to tar in both solvents, it is possible that the hydrogen used in naphthalene hydrogenation came from Scholl condensation of this substrate as dis-cussed previously. Each mole of naphthalene could lose up to 4 moles of hydrogen as a result of polymerization. This would have been more than sufficient for the observed hydrogenation. The higher conversion of naphthalene to hydrogenated products in benzene may have been due to better hydrogen shuttling ability of benzene or hydrogen released by Scholl condensation of benzene or copolymerization of benzene and naphthalene.

As a result of these experiments, cyclohexane was selected as solvent. It was evident that it would not be possible to give accurate values for conversion of the substrate to alkyl benzenes due to inter-ference of products resulting from cyclohexane reactions. However, cyclohexane was preferable to other solvents because it did not undergo

Table 3-3

Naphthalene/Solvent Reactions Using $AlCl_3$ Catalyst

Reaction Conditions: T = 225-230°C, P (H_2, at 25°C) = 1000 psig,
P (at T) = 1500-1600 psig, t = 1 hr at T

Run #	2	21
Solvent	Benzene	Cyclohexane
mole% Naphthalene	6.85	8.60
mole% $AlCl_3$	0.66	0.80
Products	Concentration (wt%)	Concentration (wt%)
alkanes	0.01	0.47
methylcyclopentane	—	1.02
cyclohexane	0.03	90.7
benzene	93.1	0.11
toluene	0.02	—
ethylbenzene	0.19	—
xylenes	0.01	—
indan	0.12	0.02
methylindans	0.02	0.01
tetralin	1.74	1.27
dihydronaphthalene	0.05	trace
methyltetralins	trace	0.10
naphthalene	4.68	6.28
alkylnaphthalenes	0.07	0.03
biphenyl	trace	—
tar	3	3
Naphthalene to Products	mole% Conversion	mole% Conversion
Total	57	51
alkylnaphthalenes	0.6	0.3
dihydronaphthalene	0.4	trace
alkyltetralins	trace	0.7
tetralin	15.5	9.5
indan & methylindans	1.3	0.1
tar	40	38

Scholl condensation or substantial cracking.

An experiment was carried out using cyclohexane and the weaker catalyst $ZnCl_2$ at 325°C and an initial hydrogen pressure of 600 psig hydrogen. No reaction was observed.

B. Selection of Reaction Time, Substrate Concentration and Catalyst to Substrate Ratio

In these experiments, reaction time, catalyst concentration and substrate concentration were varied and the effects of these variables were studied to choose representative values for the remaining experiments. In the first group of experiments, reactions were carried out at 225°C, 1000 psig initial hydrogen pressure for a reaction time of 1 hour using cyclohexane and $AlCl_3$. The concentration of the catalyst was varied from 0.5 to 5 mole%. These reactions were repeated for a reaction time of 5 hours. The reaction conditions and products are presented in Tables 3-4 and 3-5. Since there was little tar formation and solvent loss, the reported concentrations are approximately equal to wt% conversion of cyclohexane to products.

For both one hour and five hour reactions, the concentration of cyclohexane in the product mixture decreased with increase in the catalyst loading. The concentration of methylcyclopentane increased to a maximum, then decreased, while that of alkylbenzenes and alkylcyclohexanes increased with increasing catalyst loading. The extent of the reactions were higher for experiments carried out for five hours.

Similar experiments were carried out with naphthalene present. The naphthalene concentration was kept approximately constant at 9 mole% as the $AlCl_3$ concentration was varied. The reaction conditions and results are presented in Tables 3-6 and 3-7.

Table 3-4

Effect of AlCl$_3$ Concentration on Reaction of Cyclohexane for 1 Hour

Reaction Conditions: T = 225-235°C, P (H$_2$, at 25°C) = 900-1000 psig, P (at T) = 1400-1500 psig

Run #	15	3	12	13
mole% AlCl$_3$	0.41	0.82	1.50	4.71
Products	Concentration (wt%)	Concentration (wt%)	Concentration (wt%)	Concentration (wt%)
alkanes	0.62	0.72	5.53	11.7
methylcyclopentane	36.2	50.0	48.1	42.7
cyclohexane	62.6	47.6	34.8	25.6
methylcyclohexane	0.22	0.27	2.26	4.40
benzene	0.07	0.35	1.64	4.05
ethylcyclohexane	0.007	0.08	0.47	1.50
propylcyclohexane	-	0.08	0.84	-
toluene	0.007	0.04	0.31	0.41
ethylbenzene & isomers	-	-	0.23	0.31
propylbenzene & isomers	-	-	0.09	0.61
butylbenzene & isomers	0.27	0.83	5.80	9.02
wt% to tar	0	0	0	0

Table 3-5

Effect of AlCl$_3$ Concentration on Reaction of Cyclohexane for 5 Hours

<u>Reaction Conditions:</u> T = 230-235°C, P (H$_2$, at 25°C) = 900-1000 psig, P (at T) = 1400-1600 psig

Run #	16	11	17	13
mole% AlCl$_3$	0.48	0.85	1.60	4.80
Products	Concentration (wt%)	Concentration (wt%)	Concentration (wt%)	Concentration (wt%)
alkanes	0.05	12.05	8.44	11.5
methylcyclopentane	0.80	40.5	39.8	27.5
cyclohexane	99.1	26.4	25.6	20.8
methylcyclohexane	0.02	4.55	5.63	8.11
benzene	-	4.74	6.30	9.30
ethylcyclohexane	-	2.11	2.10	4.18
propylcyclohexane	-	0.30	0.46	1.07
toluene	-	0.90	1.31	2.21
ethylbenzene & isomers	-	-	0.58	1.27
propylbenzene & isomers	-	0.53	0.28	0.98
butylbenzene & isomers	0.02	7.91	7.91	13.1
wt% to tar	0	1.2	?	?

Table 3-6

Effect of AlCl$_3$ Concentration on Reaction of Naphthalene in Cyclohexane, t = 1 hr

Reaction Conditions: T = 230-232°C, P (H$_2$, at 25°C) = 1000 psig, P (atT) = 1400-1500 psig

Run #	10	21	23	22
mole% Naphthalene	10.3	8.60	8.80	8.50
mole% AlCl$_3$	0.50	0.80	1.46	4.40
mole AlCl$_3$/mole Naphthalene	0.048	0.093	0.16	0.51

Products	Concentration (wt%)	Concentration (wt%)	Concentration (wt%)	Concentration (wt%)
alkanes	0.02	0.47	0.34	0.03
methylcyclopentane	1.08	1.02	2.42	3.94
cyclohexane	88.7	90.7	91.0	90.8
methylcylohexane	–	–	0.03	0.05
benzene	0.10	0.11	0.28	0.31
toluene	–	–	0.02	0.02
ethylbenzene	–	–	0.01	0.01
propenylbenzene	–	–	0.01	–
indan	–	0.02	0.02	0.05
methylindans	–	0.01	0.02	0.05
tetralin	0.60	1.27	2.32	2.59
dihydronaphthalene	–	–	0.01	0.01
1-methyltetralin	–	0.10	0.03	0.05

Table 3-6, continued

Run #	10	21	23	22
mole $AlCl_3$/mole Naphthalene	0.048	0.093	0.16	0.51

Products	Concentration (wt%)	Concentration (wt%)	Concentration (wt%)	Concentration (wt%)
naphthalene	9.54	6.28	3.58	2.02
5-methyltetralin	—	trace	0.01	0.01
1-methylnaphthalene	0.01	0.02	0.01	0.01
2-methylnaphthalene	—	0.01	0.03	0.02
wt% to tar	0.8	2.8	4.4	2.9

Naphthalene to Products	Conversion (mole%)	Conversion (mole%)	Conversion (mole%)	Conversion (mole%)
total	37	51	74	85
alkylnaphthalenes	0.1	0.3	0.3	0.2
alkyltetralins	—	0.7	0.3	0.4
tetralin	3.8	9.5	16.5	18.6
dihydronaphthalene	—	—	0.1	0.1
tar & alkylbenzenes	33	38	57	66
(maximum alkylbenzenes)	(1.1)	(1.7)	(4.1)	(4.8)

Table 3-7

Effect of AlCl$_3$ Concentration on Reaction of Naphthalene in Cyclohexane, t = 5 hr

Reaction Conditions: T = 225-230°C, P (H$_2$, at 25°C) = 1000 psig, P (at T) = 1600 psig

Run #	24	25	26	27
mole% Naphthalene	8.90	8.90	8.80	8.60
mole% AlCl$_3$	0.42	0.70	1.50	4.40
mole AlCl$_3$/mole Naphthalene	0.047	0.079	0.17	0.51

Products	Concentration (wt%)	Concentration (wt%)	Concentration (wt%)	Concentration (wt%)
alkanes	0.31	0.32	0.37	0.05
methylcyclopentane	0.58	1.02	2.76	12.0
cyclohexane	89.1	90.4	91.3	85.7
methylcyclohexane	trace	–	0.02	0.21
benzene	0.06	0.12	0.25	0.53
toluene	–	0.01	0.02	0.14
ethylbenzene	–	–	0.02	0.09
methylethylbenzene	–	–	–	0.08
trimethylbenzene	–	–	–	0.04
propenylbenzene	–	–	0.01	0.09
butylbenzene	–	0.01	–	–

Table 3-7, continued

Run #	24	25	26	27
mole AlCl$_3$/mole Naphthalene	0.047	0.079	0.17	0.51

Products	Concentration (wt%)	Concentration (wt%)	Concentration (wt%)	Concentration (wt%)
indan	0.01	0.01	0.05	0.04
indene	0.05	–	–	–
methylindans	–	0.004	0.05	0.04
tetralin	0.48	0.71	1.93	0.83
dihydronaphthalene	–	–	0.01	0.04
1-methyltetralin	–	–	0.05	0.17
naphthalene	9.34	7.45	3.09	0.08
5-methyltetralin	–	–	0.02	0.10
1-methylnaphthalene	0.02	0.01	0.01	–
2-methylnaphthalene	–	–	0.05	–
wt% to tar	0.2	0.8	4.4	9.6

Table 3-7, continued

Run #	24	25	26	27
mole $AlCl_3$/mole Naphthalene	0.047	0.079	0.17	0.51
Naphthalene to Products	Conversion (mole%)	Conversion (mole%)	Conversion (mole%)	Conversion (mole%)
total	28	44	77	99
alkylnaphthalenes	0.2	0.1	0.4	–
alkyltetralins	–	–	0.4	1.6
tetralin	3.6	5.2	14	5.5
dihydronaphthalene	–	–	0.1	0.3
tar & alkylbenzenes	25	38	63	91
(maximum alkylbenzenes)	(1.2)	(1.7)	(4.2)	(9.9)

Comparing the results of reactions with and without naphthalene, it is observed that the reaction of cyclohexane was suppressed substantially when naphthalene was present as was discussed previously. One may assume that most of the alkylbenzenes observed in the reaction products resulted from hydrocracking of the substrate. This would account for naphthalene to alkylbenzenes conversions of 1-5% for 1 hour experiments and 1-10% for 5 hour experiments. Because of uncertainty of the above assumption, these values are reported as possible maximum conversions in Tables 3-6 and 3-7. A value which can be more accurately calculated is the sum of conversions to tar and alkylbenzenes. This value is obtained from the difference between total conversion and conversion of naphthalene to products which could not have resulted from cyclohexane reactions, namely two or more ring compounds. This value is reported in all the tables appearing in the present work when $AlCl_3$ is used as the catalyst.

For the one hour experiments, total conversion of naphthalene to products increased from 37% to 85% with increasing catalyst loading. For catalyst concentrations of 1.5% to 4.4%, corresponding to catalyst to substrate ratios of 0.2 to 0.5, the conversion was relatively constant at about 80%. Tar formation was substantial, accounting for substrate conversions of 50-60% for catalyst to substrate ratios of 0.2 to 0.5. Conversion to hydrogenated products was 17-19% and to alkylbenzenes less than 5%. Total conversions were higher for reactions at 5 hours. The conversions to hydrogenated products were the same or less, and the conversions to cracked products and tar were higher.

To study the effect of time on naphthalene hydrogenolysis, a reaction was carried out for reaction time zero. In other words, the mixture was cooled as soon as it reached the reaction temperature.

The results of this reaction are compared to similar reactions at 1 and 5 hours in Table 3-8. Substantial naphthalene conversion to products occurred during heat up time. Conversion and tar formation increased with time.

Based on results of reaction of naphthalene, it was concluded that one hour was adequate for naphthalene reaction to proceed to an extent for which observations could be made on product distributions. Since naphthalene was one of the least reactive substrates, this would assure sufficient reaction time for the other substrates. This was tested by carrying out two reactions for a more reactive substrate anthracene, for reaction times of zero and one hour. The reaction conditions and results are presented in Table 3-9. The total conversion was slightly higher for the reaction at 1 hour, 97% vs 94%. The conversion to tarry products were in the same range for both cases. For the reaction at t = 0 hr, hydrogenation proceeded to form only dihydro and tetrahydro products. For the reaction at t= 1 hr, octahydro products and ring cracking were also observed. Thus, a reaction time of one hour was chosen for the remaining experiments.

The next group of experiments was carried out to investigate the effect of substrate concentration on substrate conversion to products. One of the experiments with naphthalene at 225°C was repeated for a lower naphthalene concentration but the same catalyst to substrate ratio. Two experiments were carried out at 325°C in which the concentration of $AlCl_3$ was kept constant but the concentration of naphthalene was varied. The reaction conditions and results of these experiments are presented in Table 3-10. For experiments at 225°C, the total conversion was almost independent of the initial naphthalene concen-

Table 3-8

Effect of Time on Reaction of Naphthalene in Cyclohexane Using $AlCl_3$ Catalyst

Reactions Conditions: T = 220-232°C, P (H_2, at 25°C) = 1000 psig, P (at T) = 1400-1600 psig

Run #	103	23	26
mole% Naphthalene	8.70	8.80	8.80
mole $AlCl_3$/mole Naphthalene	0.17	0.16	0.17
t at T, hr	0	1	5

Products	Concentration (wt%)	Concentration (wt%)	Concentration (wt%)
alkanes	0.72	0.34	0.37
methylcyclopentane	1.14	2.42	2.76
cyclohexane	91.1	91.0	91.3
methylcyclohexane	0.03	0.03	0.02
benzene	0.19	0.28	0.25
toluene	trace	0.02	0.02
ethylbenzene	trace	0.01	0.02
methylethylbenzene	—	—	—
trimethylbenzene	—	—	—
propenylbenzene	—	0.01	0.01
butylbenzene	—	—	—

Table 3-8, continued

Run #	103	23	26
t at T, hr	0	1	5

Products	Concentration (wt%)	Concentration (wt%)	Concentration (wt%
indan	0.01	0.02	0.05
indene	--	--	--
methylindans	0.003	0.02	0.05
tetralin	1.36	2.32	1.93
dihydronaphthalene	--	0.01	0.01
1-methyltetralin	--	0.03	0.05
naphthalene	5.27	3.58	3.09
5-methyltetralin	0.003	0.01	0.02
1-methylnaphthalene	0.05	0.01	0.01
2-methylnaphthalene	0.005	0.03	0.05
wt% to tar	2.9	4.4	4.4

Table 3-8, continued

Run #	103	23	26
t at T, hr	0	1	5
Naphthalene to Products	Conversion (mole%)	Conversion (mole%)	Conversion (mole%)
total	60	74	77
alkylnaphthalenes	1.4	0.3	0.4
alkyltetralins	trace	0.3	0.4
tetralin	9.9	16.5	13.6
dihydronaphthalene	-	0.1	0.1
tar & alkylbenzenes	49	57	63
(maximum alkylbenzenes)	(2.5)	(4.1)	(4.2)

Table 3-9

Effect of Reaction Time on Anthracene Reaction

Reaction Conditions: solvent = cyclohexane, catalyst = $AlCl_3$,
T = 225°C, P(H_2, at 25°C) = 500 psig,
P (at T) = 800 psig

Run #	125	126
mole% Anthracene	1.51	1.51
mole $AlCl_3$/mole Anthracene	0.53	0.56
Reaction time, hr	0	1

Products	Concentration (wt%)	Concentration (wt%)
alkanes	0.05	0.36
methylcyclopentane	0.85	2.27
cyclohexane	98.4	96.5
benzene	0.002	0.005
toluene	trace	0.002
ethylbenzene	—	0.002
butylbenzene	—	0.002
diethylbenzene	0.002	0.001
indan	0.001	0.001
tetralin	0.003	0.03
dihydronaphthalene	—	0.002
1-methyltetralin	—	0.003
naphthalene	0.01	0.03
1-methylnaphthalene	0.002	0.006
2-methylnaphthalene	—	0.002
ethylnaphthalene or biphenyl	—	0.001
asym. octahydroanthracene	0.001	0.07
sym. octahydroanthracene	0.001	0.06
sym. octahydrophenanthrene	trace	0.04
tetrahydroanthracene	0.28	0.47
dihydroanthracene	0.24	0.03
anthracene	0.21	0.08
wt% to tar	1.8	1.3

Table 3-9, continued

Run #	125	126
Reaction time, hr	0	1

Anthracene to Products	Conversion (mole%)	Conversion (mole%)
total	94	97
dihydroanthracene	7.3	0.8
tetrahydroanthracene	8.5	14
asym. octahydroanth./phenan.	trace	2.0
sym. octahydroanthracene	trace	1.7
sym. octahydrophenanthrene	trace	1.7
alkylnaphthalenes	0.1	0.3
naphthalene	0.4	1.3
dihydronaphthalene	—	—
alkyltetralins	trace	0.1
tetralin	0.1	1.2
tar & alkylbenzenes	77	74
(maximum alkylbenzenes)	(0.2)	(0.6)

Table 3-10

Effect of Naphthalene Concentration on Its Reaction in Cyclohexane Using AlCl$_3$, t = 1 hr

Run #	22	202*	104*	203*
T, °C	225	226	330	325
P (H$_2$, at 25°C), psig	1000	600	800	600
P (at T), psig	1500	950	1600	1600
mole% Naphthalene	8.50	2.10	8.78	2.10
mole AlCl$_3$/mole Naphthalene	0.51	0.54	0.16	0.54

Products	Concentration (wt%)	Concentration (wt%)	Concentration (wt%)	Concentration (wt%)
alkanes	0.026	0.15	0.56	1.29
methylcyclopentane	3.94	7.80	6.22	11.5
cyclohexane	90.8	89.6	87.0	84.0
methylcyclohexane	0.053	0.17	0.17	0.45
benzene	0.31	0.17	0.25	0.46
ethylcyclohexane	–	0.012	–	0.075
toluene	0.024	0.018	0.073	0.11
ethylbenzene	0.012	0.012	0.024	0.082
methylethylbenzene	–	0.013	–	0.022
propenylbenzene	–	0.074	0.038	0.037
diethylbenzene	–	0.050	–	0.095

Table 3-10, continued

Run # .	22	202*	104*	203*
T, °C	225	226	330	325
mole% Naphthalene	8.50	2.10	8.78	2.10

Products	Concentration (wt%)	Concentration (wt%)	Concentration (wt%)	Concentration (wt%)
Indan	0.050	0.060	0.074	0.070
methylindans	0.051	0.068	0.28	0.13
tetralin	2.59	1.12	2.50	0.59
dihydronaphthalene	0.001	0.031	0.026	0.020
1-methyltetralin	0.052	0.055	0.079	0.040
naphthalene	2.02	0.38	2.28	0.64
5-methyltetralin	0.010	0.031	0.038	0.016
ethyltetralin	—	0.016	—	0.011
1-methylnaphthalene	0.010	0.023	—	0.076
2-methylnaphthalene	0.023	0.011	0.18	0.030
ethylnaphthalene or biphenyl	—	0.022	0.18	0.030
higher alkylnaphthalenes	—	0.14	—	0.036
wt% to tar	2.9	1.8	3.9	1.2

Table 3-10, continued

Run #	22	202*	104*	203*
T, °C	225	226	330	325
mole% Naphthalene	8.50	2.10	8.78	2.10

Naphthalene to Products	Conversion (mole%)	Conversion (mole%)	Conversion (mole%)	Conversion (mole%)
total	85	88	83	81
alkylnaphthalenes	0.2	4.35	2.2	5.4
dihydronaphthalene	0.10	0.93	0.20	0.60
alkyltetralins	0.40	2.52	0.50	1.70
tetralin	19	32	18	17
tar & alkylbenzenes	66	48	62	56
(maximum alkylbenzenes)	(4.8)	(18)	(6.9)	(44)

* Rapid cooling was used in these experiments.

tration. Naphthalene conversion to hydrogenated products was higher
and that to tar lower for the experiments with the initial naphthalene
concentration of 2.1% than for those with the initial naphthalene con-
centration of 8.5%. For the experiments at 325°C, conversions seemed
to be independent of the initial naphthalene concentrations in the range
investigated.

Experiments were also carried out in which the initial concentra-
tions of other substrates were varied. In Table 3-11 results of experi-
ments with tetralin and in Table 3-12 results of experiments with
phenanthrene, all at 225°C and using $AlCl_3$ catalyst, are presented. In
experiments with both substrates, conversion of substrate did not
depend substantially on initial substrate concentration in the range
investigated.

The general observation was made that when lower substrate con-
centrations were used, higher concentrations of methylcyclopentane and
alkylbenzenes were obtained in the products. Thus, at lower substrate
concentrations, the rate of reaction of cyclohexane was higher. This
resulted in interference of reaction products of cyclohexane with those
of the substrate in product analysis. However, some of the substrates,
such as anthracene and 1-naphthol, had solubilities less than 1 mole%
in cyclohexane at room temperature. So, it was desirable to choose an
initial substrate concentration not much above the saturation concen-
tration of these substrates at room temperature. Therefore, an initial
substrate concentration of 2 mole% was selected for the remaining
experiments. A catalyst to substrate ratio of 0.5 mole/mole was chosen
to be used in these experiments. As mentioned previously, because of
the interference of cyclohexane products with those of the substrate

Table 3-11

Effect of Tetralin Concentration on Its Reaction
in Cyclohexane Using $AlCl_3$, t= 1 hr

Run #	102	211*
T, °C	225	233
P (H_2, at 25°C), psig	1000	600
P (at T), psig	1300	1000
mole% Tetralin	8.70	2.11
mole% $AlCl_3$	1.48	1.11

Products	Concentration (wt%)	Concentration (wt%)
alkanes	0.044	0.43
methylcyclopentane	19.7	33.4
cyclohexane	72.8	61.2
methylcyclohexane	0.44	0.83
benzene	1.19	0.96
ethylcyclohexane	–	0.18
toluene	0.060	0.11
ethylbenzene	0.12	0.11
methylethylbenzene	0.23	0.078
trimethylbenzene	–	0.033
diethylbenzene	–	0.044
propenylbenzene	0.21	0.48
indan	0.11	0.44
methylindans	0.26	0.35
tetralin	3.77	1.08
dihydronaphthalene	0.063	0.054
1-methyltetralin	0.36	0.10
naphthalene	0.22	0.068
5-methyltetralin	0.29	0.047
ethyltetralin	–	0.006
1-methylnaphthalene	0.022	0.003
2-methylnaphthalene	0.11	0.014
wt% to tar	1.6	1.6

Table 3-11, continued

Run #	102	211*
mole% Tetralin	8.70	2.11

Tetralin to Products	Conversion (mole%)	Conversion (mole%)
total	72	67
alkylnaphthalenes	0.8	0.5
naphthalene	1.7	2.1
alkyltetralins	4.4	4.1
dimethylnaphthalene	0.5	1.7
tar & alkylbenzenes	62	59
(maximum alkylbenzenes)	(23)	(100)

*Rapid cooling was used in this experiment.

Table 3-12

Effect of Phenanthrene Concentration on Its Reactions in
Cyclohexane Using AlCl$_3$, t= 1 hr

Run #	111	113
T, °C	230	230
P (H$_2$, at 25°C), psig	1000	500
P (at T), psig	1500	800
mole% Phenanthrene	2.37	5.74
mole AlCl$_3$/mole Phenanthrene	0.46	0.41

Products	Concentration (wt%)	Concentration (wt%)
alkanes	0.043	—
methylcyclopentane	0.78	2.45
cyclohexane	96.8	91.6
benzene	0.011	0.038
toluene	0.006	0.006
ethylbenzene	0.003	0.003
trimethylbenzene	0.003	0.003
diethylbenzene	0.022	0.007
indan	0.029	0.004
methylindan	0.014	0.004
tetralin	0.089	0.130
dihydronaphthalene	0.007	0.004
1-methyltetralin	0.011	0.007
naphthalene	0.033	0.068
5-methyltetralin	0.009	0.002
1-methylnaphthalene	0.007	0.009
2-methylnaphthalene	0.004	0.004
phenylcyclohexylethane	trace	trace
ethylnaphthalene or biphenyl	0.007	0.009
asym. octahydrophenanthrene	0.041	0.072
sym. octahydroanthracene	0.073	0.058
sym. octahydrophenanthrene	0.094	0.092

Table 3-12 (continued)

Run #	111	113
mole% Phenanthrene	2.37	5.74

Products	Concentration (wt%)	Concentration (wt%)
tetrahydrophenanthrene	0.24	0.42
dihydrophenanthrene	0.29	0.57
phenanthrene	1.29	4.23
methylphenanthrenes	0.099	0.12
dimethylphenanthrenes	0.046	0.054
wt% to tar	2.5	7.2

Phenanthrene to Products	Conversion (mole%)	Conversion (mole%)
total	74	67
alkylphenanthrenes	2.4	1.2
dihydrophenanthrene	5.6	4.4
tetrahydrophenanthrene	4.7	3.2
asym. octahydrophen./anthr.	0.8	0.5
sym. octahydrophenanthrene	1.8	0.7
sym. octahydroanthracene	1.4	0.4
alkylnaphthalenes	0.7	0.1
naphthalene	0.9	0.7
dihydronaphthalene	0.2	trace
alkyltetralins	0.5	0.1
tetralin	2.4	1.4
tar & cracking	53	54
(maximum alkylbenzenes)	(2.8)	(0.9)

in reactions in the presence of $AlCl_3$, the values reported in tables for conversion of substrates to alkylbenzenes represent only maximum upper limits. A more reliable value is the sum of conversions to tar and alkylbenzenes, as discussed previously.

C.   Pressure and Temperature Variations

A group of experiments was carried out to determine the effect of hydrogen pressure and source of hydrogen in hydrogenation of naphthalene in the presence of $AlCl_3$ catalyst. This was done to choose a standard reaction pressure for the remaining experiments. The reaction conditions and results of these experiments are presented in Table 3-13. Increasing the initial hydrogen pressure did not increase the naphthalene conversion. In fact, the conversion was somewhat lower in run #105 where higher pressure was used. This could be the result of rapid cooling of the reaction mixture in this experiment, 20 min cooling time vs 90 min in experiments without rapid cooling (see Chapter 2, section II-B, Experimental Procedure). When a nitrogen atmosphere was used instead of hydrogen, the same naphthalene conversion to products was obtained. These results indicated that in the presence of $AlCl_3$ catalyst, the main source of hydrogen was the Scholl condensation of naphthalene, as discussed previously. Therefore, the hydrogen pressure did not have an effect on conversion of naphthalene in the presence of $AlCl_3$. However, to insure presence of enough hydrogen to prevent equilibrium limitation, an initial hydrogen pressure of 600 psig was selected for the substrate reactivity experiments in the presence of $ZnCl_2$ and $AlCl_3$. For initial substrate concentration of 2 mole%, this corresponded to a ratio of 50 moles of hydrogen for each mole of substrate.

The results of an experiment in which methyl cyclopentane was

Table 3-13

Effects of Pressure and Additives on Reaction of Naphthalene in Cyclohexane Using $AlCl_3$, t = 1 hr

Run #	23	105*	101*	106
mole% Naphthalene	8.80	8.60	8.50	8.80
mole $AlCl_3$/mole Naphthalene	0.160	0.175	0.165	0.189
T, °C	230	230	225	230
P (at 25°C), psig	1000 H_2	1700 H_2	1000 N_2	1000 H_2
P (at T), psig	1500	2400	1500	1400
mole% methylcyclopentane	–	–	–	15.7

Products	Concentration (wt%)	Concentration (wt%)	Concentration (wt%)	Concentration (wt%)
alkanes	0.34	0.63	0.71	0.78
methylcyclopentane	2.42	1.14	1.10	15.9
cyclohexane	91.0	90.7	91.3	75.9
methylcyclohexane	0.026	0.15	–	0.24
benzene	0.28	0.16	0.23	0.15
toluene	0.023	0.010	0.015	0.006
ethylbenzene	0.012	0.005	0.007	–
o-xylene	–	–	–	0.006
propenylbenzene	0.012	–	–	0.021
diethylbenzene	–	–	–	0.022

Table 3-13, continued

Run #	23	105*	101*	106
P (at 25°C), psig	1000 H_2	1700 H_2	1000 N_2	1000 H_2
mole% methylcyclopentane	–	–	–	15.7

Products	Concentration (wt%)	Concentration (wt%)	Concentration (wt%)	Concentration (wt%)
indan	0.024	0.016	0.015	0.056
methylindans	0.024	0.005	0.031	0.023
tetralin	2.32	1.56	2.23	2.78
dihydronaphthalene	0.013	0.005	0.016	0.012
1-methyltetralin	0.026	0.005	0.032	0.023
naphthalene	3.58	5.53	4.10	3.82
5-methyltetralin	0.013	0.005	0.016	0.023
1-methylnaphthalene	0.013	0.005	0.094	0.052
2-methylnaphthalene	0.026	0.028	0.016	0.014
ethylnaphthalene or biphenyl	–	0.027	0.095	0.070
wt% to tar	4.4	3.2	4.8	4.7

Table 3-13, continued

Run #	23	105*	101*	106
P (at 25°C), psig	1000 H_2	1700 H_2	1000 N_2	1000 H_2
mole% methylcyclopentane	–	–	–	15.7

Naphthalene to Products	Conversion (mole%)	Conversion (mole%)	Conversion (mole%)	Conversion (mole%)
total	74	58	69	72
alkylnaphthalenes	0.3	0.3	1.3	0.8
dihydronaphthalene	0.1	trace	0.1	0.1
alkyltetralins	0.3	trace	0.3	0.2
tetralin	16	11	16	20
tar & alkylbenzenes	57	47	51	51
(maximum alkylbenzenes)	(4.1)	(2.2)	(3.3)	(3.0)

*Rapid cooling was used in these experiments.

added to the reactants are also presented in Table 3-13. The purpose of this experiment was to see whether isomerization of cyclohexane had an effect on shuttling hydrogen to naphthalene. The small increase in conversion of naphthalene to tetralin was within the experimental error. Therefore, it appears that the presence of methylcyclopentane did not have a major effect on naphthalene hydrogenation.

The effect of temperature on hydrogenation of naphthalene in the presence of $AlCl_3$ was investigated in the temperature range of 25 to 350°C. The experimental conditions and results are presented in Table 3-14. Total naphthalene conversion was approximately constant at about 90% for the temperature range of 200-350°C. Above 230°C, the conversion to hydrogenated products decreased with increase in temperature. The observed ratios of tetralin to naphthalene in products were compared to equilibrium tetralin to naphthalene ratios to see if the above decrease was due to thermodynamic limitations. Wilson et al. (62) and Frye and coworkers (63,64) have determined equilibrium constants for hydrogenation of naphthalene to tetralin at elevated temperatures and pressures. Their proposed equations were based on experiments at 350-475°C and 200-1000 psig (62), or 250-460°C and 70-900 psig (63,64). A lower value for the equilibrium constant, K, is obtained from the equation proposed by Frye:

$$\log K = 6460/T - 12.40$$

in which T is in °Kelvin and K, which is in $(atm)^{-2}$, is defined as

$$K = \frac{\text{mole tetralin}}{\text{mole naphthalene}} \quad X \quad \frac{1}{P_{H_2}^2 (1 + 0.00033 \, P_{H_2}^2)^2}$$

Table 3-15 presents the equilibrium tetralin to naphthalene

Table 3-14

Effect of Temperature on Naphthalene Reaction in Cyclohexane Using AlCl$_3$ Catalyst[*]

Reaction Conditions: mole% Naphthalene = 2.1-2.2, mole AlCl$_3$/mole Naphthalene = 0.51-0.54, P (H$_2$, at 25°C) = 600 psig, t = 1 hr at T

C = Concentration

Run #	206	205	204	202	201	203	207
T°, C	25	110	170	226	264	323	348
P (at T), psig	600	700	750	950	1050	1600	1800
Products	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%
alkanes	0.062	0.059	0.040	0.15	0.19	1.29	1.97
methylcyclopentane	0.044	0.24	3.40	7.80	9.60	11.5	18.1
cyclohexane	96.6	97.1	94.5	89.6	87.8	84.0	75.9
methylcyclohexane	–	trace	0.095	0.17	0.16	0.45	0.74
benzene	0.011	0.048	0.19	0.17	0.32	0.46	0.74
ethylcyclohexane	–	–	–	0.012	0.023	0.075	0.19
propylcyclohexane	–	–	–	–	–	0.035	0.036
toluene	–	trace	0.005	0.018	0.058	0.11	0.23
ethylbenzene	–	–	–	0.012	0.020	0.082	0.25
o-xylene	–	–	0.003	–	–	0.015	0.043
methylethylbenzene	–	–	0.003	0.013	0.018	0.037	0.10
propylbenzene	–	trace	–	0.002	0.008	0.028	0.10
propenylbenzene	–	0.005	0.049	0.074	0.0078	0.095	0.19
diethylbenzene	–	0.019	0.041	0.050	0.035	0.018	0.11
idan	–	0.019	0.030	0.060	0.070	0.070	0.22
methylindans	–	–	0.029	0.068	0.10	0.13	0.078
tetralin	trace	0.42	1.03	1.12	1.16	0.59	0.39

Table 3-14, continued

C = Concentration

Run #	206	205	204	202	201	203	207
T, °C	25	110	170	226	264	323	348
Products	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%
dihydronaphthalene	-	trace	0.017	0.031	0.046	0.020	0.014
1-methyltetralin	-	-	0.020	0.055	0.089	0.040	0.026
naphthalene	3.24	1.89	0.74	0.38	0.39	0.63	0.26
5-methyltetralin	-	-	0.015	0.031	0.024	0.016	0.016
ethyltetralin	-	-	trace	0.016	0.026	0.011	0.010
1-methylnaphthalene	0.002	0.002	0.015	0.023	0.040	0.076	0.057
2-methylnaphthalene	-	0.001	0.004	0.010	0.011	0.030	0.023
ethylnaphthalene or biphenyl	-	0.004	0.019	0.022	0.020	0.074	0.071
higher alkylnaphthalenes	-	0.25	0.12	0.14	0.061	0.036	0.042
wt% to tar	0	1.5	2.0	1.8	1.9	1.2	1.5

Table 3-14, continued

X = Conversion

Run #	206	205	204	202	201	203	207
T, °C	25	110	170	226	264	323	348

Naphthalene to Products	X,mole%	X,mole%	X,mole%	X,mole%	X,mole%	X,mole%	X,mole%
total	0-1.0	44	78	88	88	81	92
alkylnaphthalenes	—	5.0	3.5	4.3	3.2	5.4	4.3
dihydronaphthalene	—	trace	0.5	0.93	1.4	0.60	0.40
alkyltetralins	—	—	0.9	2.5	3.0	1.7	1.3
tetralin	trace	12	28	33	34	17	11
tar & alkylbenzenes	0-1	27	46	48	47	56	75
(maximum alkylbenzenes)	(0)	(3.8)	(12)	(18)	(28)	(44)	(81)

*
Rapid cooling was used in these experiments.

Table 3-15*

Comparison of Equilibrium to Observed Tetralin to Naphthalene Ratios

| Run # | T, °C | K, atm^{-2} | mole tetralin / mole naphthalene | |
			equilibrium	observed
202	226	3.5	15000	2.7
201	264	0.43	2000	2.8
203	323	0.027	300	0.9
207	348	0.010	140	1.4

*The reaction conditions and products for these experiments are presented in Table 3-14.

ratios as well as the observed tetralin to naphthalene ratios. The equilibrium ratios were much higher than the observed ratios. Thus, the observed decrease in conversion to tetralin was not due to equilibrium limitations. Rather, it corresponded to an increase in the rate of conversion of hydrogenated products to cracked and polymerized products. Noting that the wt% conversion of initial reactants to tar did not increase in this temperature range, it may be assumed that the tar formation was relatively constant in this temperature range. This would correspond to substantial increase in conversion of naphthalene to alkylbenzenes with increase in temperature in the temperature range of 230-350°C. The temperature of 325°C was selected as the reaction temperature for the substrate reactivity experiments.

II. The Substrate Reactivity Experiments in the Presence of $ZnCl_2$

These experiments were carried out to provide information regarding relative reactivity of different structures in the presence of $ZnCl_2$ catalyst. Two and three fused ring aromatic compounds presented in Table 1-2 in the introduction were used as substrates. Cyclohexane was used as solvent and $ZnCl_2$ as catalyst. The experimental procedure for these experiments is given in Chapter 2, section II-B.

A. Reactions of Two-Ring Compounds

The reaction conditions, product distribution and conversion of substrates to products are presented in Table 3-16. As mentioned in the section on Preliminary Experiments, cyclohexane did not react under these reaction conditions. Therefore, there was no solvent interference in these reactions. No tar formation or gasification was observed in any of the reactions in the presence of $ZnCl_2$.

Naphthalene was not very reactive under these reaction conditions,

Table 3-16

Reactions of Two-Ring Compounds in the Presence of ZnCl$_2$

<u>Reaction Conditions:</u> solvent = cyclohexane, substrate concentration = 2.0-2.2 mole%.
mole ZnCl$_2$/mole Substrate = 0.54, T = 25°C, P (H$_2$, at 25°C) = 600 psig,
P (at T) ≅ 1600 psig, t = 1 hr at T

C = Concentration

Run #	152	151	142	145	143	146	246
Substrate	(structure)	(structure)	(structure)	CH$_3$ (structure)	OH (structure)	OH (structure)	OH (structure)

Products	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%
cyclohexane	96.7	96.7	99.6	99.6	98.4	97.9	97.4
toluene	-	0.001	0.001	0.001	0.002	0.005	0.009
o-xylene	-	-	-	0.003	-	-	-
ethylbenzene	-	-	trace	0.001	-	-	0.001
propylbenzene & isomers	-	-	-	-	trace	0.015	-
decalin	-	-	0.018	-	-	0.017	-
indan	-	0.001	0.005	-	-	-	0.002
methylindans	-	0.004	0.002	0.001	0.001	0.018	0.006
tetralin	0.017	2.09	3.34	0.034	0.45	0.013	2.07
dihydronaphthalene	0.002	0.45	-	0.002	0.069	-	0.016
1-methyltetralin	-	-	-	0.091	-	-	-
naphthalene	3.28	0.65	0.012	0.008	0.10	0.001	0.37
dimethyltetralin	-	-	-	0.040	-	-	-

- continued on next page -

Table 3-16, continued

C = Concentration

Run #	152	151	142	145	143	146	246
Substrate	⬡⬡	⬡⬡	⬡⬡	CH₃ ⬡⬡	OH ⬡⬡	OH ⬡⬡	OH ⬡⬡
Products	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%
1,2,3,4-tetrahydro-1-naphthol	-	-	-	-	0.006	0.001	0.008
1-methylnaphthalene	trace	0.021	-	3.15	-	0.001	trace
1-tetralone	-	-	-	-	0.13	0.001	trace
other alkylnaphthalenes	-	-	0.003	0.009	-	-	-
5,6,7,8-tetrahydro-1-naphthol	-	-	-	-	0.074	1.94	0.026
5,6,7,8-tetrahydro-2-naphthol	-	-	-	-	-	0.046	-
1-naphthol	-	-	-	-	0.080	-	0.035
2-naphthol	-	-	-	-	-	0.046	-

Table 3-16, continued

X = Conversion

Run #	152	151	142	145	143	146	246
Substrate	(naphthalene)	(dihydronaphthalene)	(tetralin)	CH₃ (methyl-naphthalene)	OH (naphthol)	OH (naphthol)	OH (naphthol)
Substrate to Products	X,mole%	X,mole%	X,mole%	X,mole%	X,mole%	X,mole%	X,mole%
total	0.6	81	1.3	6	25	4	80
alkylbenzenes	–	0.2	0.2	0.3	0.1	1.3	0.6
decalin	–	–	0.6	–	–	0.5	–
tetralin	0.5	61	(99)	1.1	14	0.4	66
alkyltetralins	–	–	–	3.6	–	–	–
dihydronaphthalene	0.06	(16)	–	0.07	2.1	–	0.5
naphthalene	(96)	19	0.4	0.25	3.4	0.03	12
1-methylnaphthalene	–	–	–	92	–	0.02	–
other alkylnaphthalenes	–	0.5	0.1	0.4	–	–	–
1-tetralone	–	–	–	–	3.5	0.01	–
1,2,3,4-tetrahydro-1-naphthol	–	–	–	–	0.1	0.01	trace
5,6,7,8-tetrahydro-1-naphthol	–	–	–	–	2.1	(sat.)	0.7
5,6,7,8-tetrahydro-2-naphthol	–	–	–	–	–	1.4	–
1-naphthol	–	–	–	–	(sat.)	–	1.0

giving a total conversion of 0.6% to hydrogenated products. The presence of the electron releasing methyl group in 1-methylnaphthalene increased the total conversion to 6%. The conversion was mostly to hydrogenated products (alkyltetralins). Some substituent removal was also observed (tetralin and naphthalene). The presence of the strongly electron releasing hydroxyl group in 1-naphthol increased the total conversion to 25%. The products were mostly those of hydrogenation and substituent removal.

The reactivity of the partially hydrogenated products of the above compounds varied. Dihydronaphthalene, the first product of partial hydrogenation of naphthalene, was found to be very reactive under these reaction conditions. The total conversion of this substrate to products was 81%, of which 61% was hydrogenation to tetralin and 19% was dehydrogenation to naphthalene. Tetralin, the second product of partial hydrogenation of naphthalene, was not very reactive. Among the two partially hydrogenated products of naphthol, 1,2,3,4-tetrahydro-1-naphthol was found to be very reactive. It gave a total conversion of 80%, of which 66% was to tetralin and 12% was to naphthalene. The other intermediate, 5,6,7,8-tetrahydro-1-naphthol, was not very reactive. However, ring cracking of this substrate to give alkylbenzenes as final products, was observed.

B. Reactions of Three-Ring Compounds

The reaction conditions, product distributions and conversion of substrates to products are presented in Table 3-17. As mentioned in section A, there was no solvent interference in these reactions. No tar formation or gasification was observed.

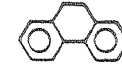Anthracene was the most reactive of the three ring compounds

Table 3-17

Reactions of Three-Ring Compounds in the Presence of $ZnCl_2$

Reaction Conditions: solvent = cyclohexane, substrate concentration = 2.0-2.2 mole%, mole $ZnCl_2$/mole substrate = 0.54, T = 325 °C, P (H_2 at 25 °C) = 600 psig, P (at T) = 1600 psig, t = 1 hr at T
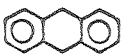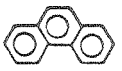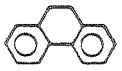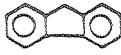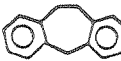
C = Concentration

Run #	147	141	150	110*	148	149	144
Substrate							
Products	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%
cyclohexane	96.7	96.1	95.6	93.3	95.9	96.9	95.7
toluene	trace	0.001	0.012	0.003	0.013	–	0.001
ethylbenzene	0.001	–	–	–	–	–	–
tetralin	–	–	–	0.003	–	–	–
naphthalene	–	–	–	0.007	–	–	–
ethylnaphthalene	0.005	–	–	0.003	–	–	0.001
biphenyl	–	–	–	–	–	–	–
propylnaphthalene	–	0.001	–	0.003	–	–	–
bibenzyl	–	–	–	–	–	–	0.002
butyltetralin	–	0.001	–	–	0.003	–	
{ asym. octahydroanthracene/ asym. octahydrophenanthrene/ butyldihydronaphthalene	0.019	0.025	–	0.007	–	–	

Table 3-17, continued

C = Concentration
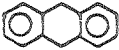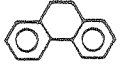
Run #	147	141	150	110*	148	149	144
Substrate							
Products	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%
2-ethyldiphenylmethane	–	–	–	–	–	–	0.026
2-methylbibenzyl	–	–	–	–	–	–	0.077
sym. octahydroanthracene	0.122	0.072	4.3	–	–	–	–
sym. octahydrophenanthrene	–	0.005	trace	0.027	0.019	–	–
tetrahydroanthracene/ tetrahydrophenanthrene	0.57	0.22	–	0.023	0.014	–	–
dihydroanthracene/ dihydrophenanthrene	2.27	3.34	trace	0.12	4.0	–	–
anthracene/phenanthrene	0.31	0.19	–	6.3	0.072	–	–
fluorene	–	–	–	–	–	4.1	–
dihydrodibenzocycloheptene	–	–	–	–	–	–	4.0

Table 3-17, continued

X = Conversion

Run #	147	141	150	110*	148	149	144
Substrate							
Substrate to Products	X,mole%	X,mole%	X,mole%	X,mole%	X,mole%	X,mole%	X,mole%
total	68	12	trace	1.4	2.4	0	3.3
alkylbenzenes	trace	trace	0.6	trace	0.6	–	0.1
tetralin	–	–	–	trace	–	–	–
alkyltetralins	–	trace	–	—	trace	–	–
naphthalene	–	–	–	0.1	–	–	–
alkylnaphthalenes	0.1	0.6	–	0.1	trace	–	–
alkyl(bibenzyls/biphenyls)	–	–	–	–	–	–	3.3
asym. octahydroanthracene/ asym. octahydrophenanthrene/ butyldihydronaphthalene	0.4	0.5	–	0.1	–	–	–
sym. octahydroanthracene	3.2	1.6	(99)	–	–	–	–
sym. octahydrophenanthrene	–	0.1	trace	0.2	0.4	–	–
tetrahydroanthracene/ tetrahydrophenanthrene	13	5.2	—	0.2	0.3	–	–
dihydroanthracene/ dihydrophenanthrene	51	(79)	trace	0.9	(94)	–	–
anthracene/phenanthrene	(sat.)	4.6	–	(sat.)	1.7	–	–
fluorene	–	–	–	–	–	(100)	–
dihydrodibenzocycloheptene	–	–	–	–	–	–	(88)

*Reaction conditions for this experiment were: substrate concentration = 6.5 mole%, mole $ZnCl_2$/mole substrate = 0.82

investigated, undergoing a total conversion of 68%. The conversion was mostly to dihydroanthracene and to a lesser extent to tetrahydro-anthracene and octahydroanthracene. Little cracking of the side rings was observed. The conversion of phenanthrene was 1.4%, higher than that for naphthalene, but much lower than that for anthracene. Again the hydrogenation was mostly to the dihydro product. However, the difference between the conversion to dihydro versus tetrahydro and octahydro derivatives was not as substantial as that of anthracene. The order of reactivity observed for the simple unsaturated compounds in the presence of $ZnCl_2$ was anthracene $\gg$ phenanthrene $>$ naphthalene.

The first hydrogenation intermediate of anthracene, dihydro-anthracene, gave a total conversion of 12% to products. This included further hydrogenation to tetrahydro and octahydro derivatives as well as dehydrogenation to anthracene. Octahydroanthracene was not reactive under these reaction conditions. Dihydrophenanthrene was less reactive than dihydroanthracene. The total conversion of the above compound was 2.4%, mostly due to dehydrogenation to phenanthrene.

Runs #141, 148, 149 and 144 may be compared to see the effect of the size of the central saturated ring on its cracking. No cracking occurred, under the reaction conditions used, for a ring with five carbons, as observed in the reaction of fluorne. There was also no cracking of the central ring when this ring had 6 carbons, as observed in the reactions of dihydroanthracene and dihydrophenanthrene. However, for dihydrodibenzocycloheptene, which contained seven carbons in the central ring, cracking of this ring was observed.

C. Source of Hydrogen

The hydrogen used in hydrogenation and cracking of each sub-

strate may come from one of three sources: 1 - molecular hydrogen, 2 - polymerization of the substrate, and 3 - dehydrogenation of the solvent. The experiments reported in this section were undertaken to determine which of the above sources was dominant.

The experiments with 1-naphthol and anthracene were repeated using nitrogen gas instead of hydrogen. The reaction conditions, product distributions and conversion of substrates to products are given in Tables 3-18 and 3-19. For purpose of comparison, the results of experiments with the above compounds in which hydrogen gas was used are also presented in these tables. The total conversion of naphthol to liquid products was reduced from 25% to 4% in the absence of hydrogen. Conversion to tetralin, which was a major product when hydrogen gas was used, was minimal in the absence of hydrogen. The total conversion of anthracene to liquid products was reduced from 68% to less than 1% in the absence of hydrogen. The only product observed in this case was dihydroanthracene. Substantial polymerization of both substrates occurred in the absence of hydrogen.

These results indicate that the source of the hydrogen used in hydrogenation of the fused ring aromatic compounds was molecular hydrogen when the reactions were catalyzed by $ZnCl_2$. Polymerization of the substrate may have provided additional hydrogen, but the proportion from this source was very small compared to the above source. Since cyclohexane did not react in the presence of $ZnCl_2$, this solvent did not act as a source of hydrogen in the presence of $ZnCl_2$.

III. The Substrate Reactivity Experiments in the Presence of $AlCl_3$

These experiments were carried out to provide information regarding relative reactivity of different structures in the presence

Table 3-18

Source of Hydrogen in Reaction of 1-Naphthol in Cyclohexane
in the Presence of $ZnCl_2$

Reaction Conditions: mole% naphthol = 2.0, mole $ZnCl_2$/mole
naphthol = 0.54, T = 325°C, P (at 25°C) =
600 psig, P (at T) = 1600 psig, t = 1 hr at T

Run #	143	243
Gas	Hydrogen	Nitrogen
Products	Concentration (wt%)	Concentration (wt%)
cyclohexane	98.4	99.4
toluene	0.002	0.001
propylbenzene	trace	—
methylindan	0.001	—
tetralin	0.45	0.004
dihydronaphthalene	0.069	0.005
naphthalene	0.105	0.050
1-tetralone	0.13	0.056
1,2,3,4-tetrahydro-1-naphthol	0.006	trace
5,6,7,8-tetrahydro-1-naphthol	0.074	trace
1-naphthol	0.80	0.65
2-naphthol	—	0.010

Naphthol to Products	Conversion (mole%)	Conversion (mole%)
total (liquid)	25	4
alkylbenzenes	0.1	—
tetralin	14	0.1
dihydronaphthalene	2.1	0.2
naphthalene	3.4	1.6
1-tetralone	3.5	1.6
1,2,3,4-tetrahydro-1-naphthol	0.1	trace
5,6,7,8-tetrahydro-1-naphthol	2.1	trace
1-naphthol	(sat.)	(19)
2-naphthol	—	0.3
polymerization		77

Table 3-19

Source of Hydrogen in Reaction of Anthracene in
Cyclohexane in the Presence of $ZnCl_2$

Reaction Conditions: mole% anthracene = 2.1, mole $ZnCl_2$/mole
anthracene = 0.54, T = 325°C, P (at
25°C) = 600 psig, P (at T) = 1600 psig,
t = 1 hr at T

Run #	147	247
Gas	Hydrogen	Nitrogen
Products	Concentration (wt%)	Concentration (wt%)
cyclohexane	96.7	99.7
toluene	trace	0.002
ethylbenzene	0.001	0.002
tetralin	—	trace
naphthalene	—	trace
ethylnaphthalene	0.005	—
butylnaphthalene	0.018	—
octahydroanthracene	0.122	—
tetrahydroanthracene	0.57	trace
dihydroanthracene	2.27	0.039
anthracene	0.31	0.21

Anthracene to Products	Conversion (mole%)	Conversion (mole%)
total (liquid)	68	0.9
alkylbenzenes	trace	0.1
tetralin	—	trace
naphthalene	—	trace
alkylnaphthalenes	0.4	—
octahydroanthracene	3.2	—
tetrahydroanthracene	13	trace
dihydroanthracene	51	0.9
anthracene	(7)	(5)
polymerization		94

of the stronger catalyst, $AlCl_3$. The reaction procedure, solvent and
substrates used were the same as those of the substrate reactivity
experiments in the presence of $ZnCl_2$.

The gaseous products of some of the experiments in the presence
of $AlCl_3$ catalyst were analyzed by GC. The results of the analyses are
presented in Table 3-20, together with results of some of the reactions
in the preliminary section. Gasification was minimal at 225°C, but at
325°C gasification to the extent of 3-10% took place. This number is
based on the assumption that each mole of substrate produced one mole
of gas, and that there was no cyclohexane gasification. Since each
mole of substrate could produce more than one mole of gas, the conversion
of substrates to gases was lower by a factor of two or more than the
reported values. The value would be even lower if cyclohexane gasifi-
cation occurred. Thus, the conversion of substrates to gaseous products
was probably in the order of a few percent or less, and was omitted in
the calculations.

A. Reactions of Two-Ring Compounds

The reaction conditions, product distribution and conversion of
substrates to products are presented in Table 3-21. Cyclohexane
reacted under these reaction conditions. The product distribution of
reaction of cyclohexane is also given in Table 3-21. The product
contained 44% methylcyclopentane as well as one ring aromatic and
aliphatic compounds in concentrations as high as a few percent. A small
amount of tar was also formed. In the presence of substrates, the
reaction of cyclohexane was suppressed. However, it was not possible
to distinguish the alkylbenzene products resulting from the reaction of
substrates from those of cyclohexane. Therefore, the value calculated

Table 3-20

Conversion of Substrates to Gases in the Presence of $AlCl_3$

Reaction Conditions: solvent = cyclohexane, P (H_2, at 25°C) = 500-800 psig, P (at T) = 800-1800 psig
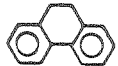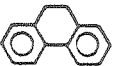
X = Conversion
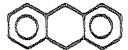
Run #	23	115	116	125	126	123
Substrate	(structure)	(structure)	(structure)	(structure)	(structure)	(structure)
T, °C	225	225	325	225	225	325
t (at T), hour	1	1	1	0	1	1
Conversion to Gases	X, mole%	X, mole%	X, mole%	X, mole%	X, mole%	X, mole%
total	trace	0.3	10	0.6	0.3	3
CH_4	trace	0.1	1.3	trace	0.1	0.6
C_2H_6	—	—	0.1	—	—	0.1
C_2H_4	—	—	0.1	—	—	0.2
C_3H_8	trace	0.1	0.2	0.1	—	1.9
C_3H_6	trace	0.1	8.3	0.5	0.2	0.3

Table 3-21

Reactions of Two-Ring Compounds in the Presence of $AlCl_3$

Reaction Conditions: solvent = cyclohexane, substrate concentration = 2.0-2.2 mole%, mole $AlCl_3$/mole substrate = 0.54, T = 325°C, P (H_2, at 25°C) = 600 psig, P (at T) = 1600 psig, t = 1 hr at T

C = Concentration

Run #	130	203	138	131	137	135	136	234
Substrate	—	(naphthalene)	(tetralin)	(decalin)	CH_3 (methyl)	OH	OH	OH
Products	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%
alkanes	7.95	1.29	2.32	2.47	1.30	0.033	0.030	0.13
methylcyclopentane	44.1	11.5	15.2	34.6	11.5	1.49	1.30	0.32
cyclohexane	36.1	84.0	78.6	56.8	83.8	97.8	97.2	97.3
methylcyclohexane	3.88	0.40	0.86	1.52	0.65	—	—	—
benzene	2.33	0.46	0.88	1.54	0.50	0.004	—	0.034
ethylcyclohexane	0.96	0.075	0.16	0.36	0.14	0.016	—	—
propylcyclohexane	1.11	0.035	—	—	—	—	0.001	—
toluene	0.70	0.11	0.30	0.45	0.22	0.016	—	0.011
ethylbenzene	—	0.082	0.23	0.39	—	0.004	0.010	0.004
hydrindan	—	—	—	—	—	—	0.036	—
o-xylene	0.44	0.015	0.042	0.065	0.15	0.001	—	0.002
propylbenzene/decalin	0.14	0.022	—	—	0.030	—	0.044	—
methylethylbenzene/decalin	—	0.037	0.096	0.19	0.073	0.001	0.079	0.002
trimethylbenzene	0.31	0.028	0.44	—	—	—	—	—

Table 3-21, continued

C = Concentration

Run #	130	203	138	131	137	135	136	234
Substrate	—	(structure)	(structure)	(structure)	CH₃ (structure)	OH (structure)	OH (structure)	OH (structure)
Products	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%
butylbenzene	0.46	–	–	0.19	–	0.015	–	0.003
propenylbenzene	–	0.095	0.16	0.34	–	–	–	–
diethylbenzene	0.55	0.018	–	0.90	–	0.010	–	0.001
indan	0.32	0.070	0.10	0.18	0.10	0.005	0.009	0.003
indene	0.46	–	–	–	0.094	–	–	–
methylindans	0.23	0.13	0.18	0.12	0.18	0.009	0.015	0.008
tetralin	–	0.59	0.47	0.23	0.071	0.11	0.46	1.70
dihydronaphthalene	–	0.020	0.013	0.035	–	0.008	–	0.001
1-methyltetralin	–	0.040	0.044	0.076	0.17	–	–	–
naphthalene	–	0.63	0.13	0.081	0.12	0.13	0.10	0.44
phenol	–	–	–	–	–	–	0.002	
5-methyltetralin	–	0.016	0.011	0.023	0.17	0.002	–	–
dimethyltetralin	–	0.011	0.006	0.020	–	–	–	–
1,2,3,4-tetrahydro-1-naphthol	–	–	–	–	–	trace	–	trace
1-methylnaphthalene	–	0.076	0.031	0.035	0.15	0.003	0.009	0.003
2-methylnaphthalene	–	0.030	0.009	0.015	0.009	0.002	–	–
dimethylnaphthalene/biphenyl	–	0.073	0.019	0.036	0.15	0.006	–	0.002
biphenylmethane	–	–	–	–	0.24	–	–	–
bibenzyl	–	–	–	–	0.056	–	–	–

Table 3-21, continued

C = Concentration

Run #	130	203	138	131	137	135	136	234
Substrate	—	(naphthalene)	(methylnaphthalene/alkyl)	(decalin/tetralin)	(methyl CH₃ naphthalene)	(OH naphthol)	(OH naphthol)	(OH naphthol)
Products	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%
1-tetralone	-	-	-	-	-	0.070	0.016	-
propenylphenol	-	-	-	-	-	-	0.033	-
butenylphenol	-	-	-	-	-	-	0.030	-
5,6,7,8-tetrahydro-1-naphthol	-	-	-	-	-	0.003	0.38	0.016
5,6,7,8-tetrahydro-2-naphthol	-	-	-	-	-	-	0.25	-
higher alkylnaphthalenes	-	0.036	-	-	-	0.011	-	0.002
1-naphthol	-	-	-	-	-	0.20	-	-
wt% to tar	0.4	1.2	1.3	1.3	0.9	-	-	-

Table 3-21, continued

X = Conversion

Run #	130	203	138	131	137	135	136	234
Substrate	—	(naphthalene)	(dihydronaphthalene)	(tetralin)	(methyl-naphthalene, CH_3)	(naphthol, OH)	(hydroxy-tetralin, OH)	(hydroxy-tetralin, OH)
Substrate to Products	X,mole%	X,mole%	X,mole%	X,mole%	X,mole%	X,mole%	X,mole%	X,mole%
total	—	81	97	93	96	94	89	100
decalin[a]	—	—	3	6	3	trace	4	—
tetralin	—	17	13	(7)	2.1	3.4	15	55
dihydronaphthalene	—	0.6	(0.4)	1.0	—	0.3	—	trace
alkyltetralins	—	1.7	1.5	3.1	9.2	trace	—	—
naphthalene	—	(19)	3.7	2.5	3.6	4.2	3.4	15
1-methylnaphthalene	—	2.1	0.8	1.0	4.2	0.1	0.3	0.1
other alkylnaphthalenes	—	3.3	.6	1.3	3.0	0.5	—	—
biphenylalkanes	—	—	—	—	9.1	—	—	—
alkylphenols	—	—	—	—	—	—	2.1	—
1-tetralone	—	—	—	—	—	2.0	0.5	—
1,2,3,4-tetrahydro-1-naphthol	—	—	—	—	—	trace	trace	trace
5,6,7,8-tetrahydro-1-naphthol	—	—	—	—	—	0.1	11	0.5
5,6,7,8-tetrahydro-2-naphthol	—	—	—	—	—	—	7.3	—
1-naphthol	—	—	—	—	—	(5.7)	—	—
tar & alkylbenzenes	—	56	77	84	64	84	56	30
(maximum alkylbenzenes)	—	(44)	(84)	(100)	(54)	(3)	(4)	(3)

[a]The conversions reported for decalin are only approximations due to overlapping of GC peaks of decalins and alkylbenzenes.

for conversion of substrates to alkylbenzenes, which was based on the
concentration of alkylbenzenes in the product mixture, was usually much
higher than the actual conversion. This number is only reported as an
upper limit. The number reported for conversion of substrate to tar
plus alkylbenzenes is a more reliable value (see also Chapter 3,
section I-B).

As in the case where $ZnCl_2$ was used as catalyst, naphthalene was
the least reactive of the two-ring compounds, with a total conversion
of 81%. Of this amount, 56% was converted to tar and alkylbenzenes.
Tetralin was a major product in the liquid phase. The presence of
electron releasing methyl and hydroxyl groups enhanced the reactivity
of the substrate. The effect was not as substantial as that observed
with the weaker catalyst, $ZnCl_2$, due to high reactivity of all sub-
strates in the presence of $AlCl_3$. The products of partial hydrogenation
of naphthalene, dihydronaphthalene and tetralin, were both reactive,
with conversions of over 90%. Substantial conversions to tar and alkyl-
benzenes were observed in the reactions of both compounds, 74% for di-
hydronaphthalene and 84% for tetralin. Since the wt% conversion of
substrate to tar was approximately the same for naphthalene, dihydro-
naphthalene and tetralin, it may be assumed that the above increase in
conversion to tar and cracking was mostly due to ring cracking and not
tar formation. With this assumption, the cracking of dihydronaphthalene
and tetralin could have been 20-30% higher than that of naphthalene.

It is interesting to note that in reactions of naphthol and its
hydrogenated derivatives, the concentration of methylcyclopentane and
alkylbenzenes were much lower than those in the reaction of other
substrates. This is the most evident for the reaction of 1,2,3,4-

tetrahydro-1-naphthol, run #234. It was observed that this compound reacted substantially in the presence of the weaker catalyst $ZnCl_2$ to produce naphthalene and tetralin. Naphthalene and tetralin were found to be quite reactive in the presence of $AlCl_3$. Thus, the hydrogenation of tetrahydrnaphthol was expected to proceed through rapid conversion to naphthalene and tetralin followed by conversion of these compounds to alkylbenzenes and tar. The presence of large amounts of naphthalene and tetralin and low concentrations of alkylbenzenes in the product mixture of reaction of 1,2,3,4-tetrahydro-1-naphthol could be due to deactivation of the catalyst, $AlCl_3$, by the water released in formation of naphthalene and tetralin. The same could hold true for the reactions of 1-naphthol and 5,6,7,8-tetrahydro-1-naphthol. This could also explain the absence of tar in the recovered products.

B. Reactions of Three-Ring Compounds
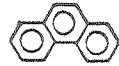
The reaction conditions, product distribution and conversion of substrates to products are presented in Table 3-22. The product distribution of reaction of cyclohexane is also given in Table 3-22 (see Chapter 3, section III-B). All three-ring compounds studied were quite reactive under these conditions. This resulted in substantial tar formation and cracking to alkylbenzenes. Anthracene reacted to the extent of 99.8% conversion. Dihydro and octahydro derivatives of anthracene also reacted to large extents. Thus, small amounts of hydrogenated intermediates were observed in the product mixture of reaction of anthracene. The order of reactivity for simple unsaturated compounds using $AlCl_3$ and the present reaction conditions was anthracene > phenanthrene >> naphthalene. Concentrations of hydrogenated intermediates of phenanthrene were also low in the product

Table 3-22

Reactions of Three-Ring Compounds in the Presence of AlCl₃

Reaction Conditions: solvent = cyclohexane, substrate concentration = 2.0-2.2 mole%, mole AlCl₃/mole substrate = 0.54, T = 325°C, P (H₂, at 25°C) = 600 psig, P (at T) = 1600 psig, t = 1 hr at T

C = Concentration

Run #	130	232	134	139	112	116	133	132
Substrate	—	(structure)	(structure)	(structure)	(structure)	(structure)	(structure)	(structure)
Products	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%
alkanes	7.95	0.39	0.82	3.22	0.60	1.06	2.60	1.47
methylcyclopentane	44.1	6.7	7.6	19.2	7.1	9.0	21.5	6.4
cyclohexane	36.1	91.9	89.5	73.0	89.6	87.8	72.0	88.7
methylcyclohexane	3.88	0.14	0.46	1.24	—	—	1.00	—
benzene	2.33	0.11	0.29	0.96	0.35	0.39	0.84	0.66
ethylcyclohexane	0.96	0.035	0.18	0.31	0.11	0.11	—	—
propylcyclohexane	1.11	—	—	—	—	—	—	—
toluene	0.70	0.063	0.13	0.38	0.16	0.15	0.28	0.40
ethylbenzene	—	0.064	0.084	0.33	0.12	0.13	0.23	0.37
o-xylene	0.44	0.010	0.012	0.061	0.031	0.030	0.045	0.058
propylbenzene	0.14	0.019	0.028	0.16	—	—	—	—
methylethylbenzene	—	—	—	—	—	0.054	0.10	0.14
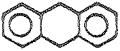
Table 3-22, continued

C = Concentration

Run #	130	232	134	139	112	116	133	132
Substrate	—	(structure)	(structure)	(structure)	(structure)	(structure)	(structure)	(structure)
Products	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%
trimethylbenzene	0.31	0.010	—	—	0.069	—	0.070	0.15
butylbenzene	0.46	—	0.023	0.19	0.070	0.008	0.071	0.12
diethylbenzene	0.55	0.033	0.039	0.16	0.079	0.063	0.071	0.13
indan	0.32	0.033	0.036	0.11	0.080	0.073	—	—
indene	0.46	0.020	0.015	0.083	0.038	0.017	—	—
methylindans	0.23	0.043	0.064	0.083	0.053	0.059	0.11	—
tetralin	—	0.17	0.17	0.18	0.099	0.10	0.024	0.063
dihydronaphthalene	—	0.017	0.019	0.020	0.010	0.010	—	—
1-methyltetralin	—	0.041	0.041	0.050	0.030	0.041	0.019	0.006
naphthalene	—	0.055	0.072	0.062	0.059	0.064	—	0.009
5-methyltetralin	—	0.010	0.013	0.023	0.007	0.012	—	—
dimethyltetralin	—	0.026	0.015	0.010	0.004	0.006	0.012	—
1-methylnaphthalene	—	0.016	0.024	0.018	0.030	0.035	0.012	—
2-methylnaphthalene	—	0.010	0.015	0.007	0.011	0.016	0.25	—
phenylcyclohexylethane	—	0.009	0.013	—	0.002	0.022	—	—
biphenyl/ ethyl(or dimethyl)naphthalene	—	0.032	0.038	0.015	0.034	0.035	0.25	0.013
diphenylmethane/butyltetralin	—	0.007	0.009	0.009	0.019	0.027	0.024	0.013

Table 3-22, continued

C = Concentration
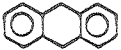
Run #	130	232	134	139	112	116	133	132
Substrate	—	(structure)	(structure)	(structure)	(structure)	(structure)	(structure)	(structure)
Products	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%
butylhydronaphthalene/ asym. octahydroanthracene/ asym. octahydrophenanthrene/ bibenzyl	–	0.024	0.054	–	0.053	0.024	–	0.75
2-methylbiphenyl	–	–	–	–	–	–	0.20	–
2-ethylbiphenyl	–	–	–	–	–	–	0.082	–
butylnaphthalene	–	0.004	0.013	0.003	0.019	0.024	–	–
2-ethyldiphenylmethane	–	–	–	–	–	–	–	0.36
2-methylbibenzyl	–	–	–	–	–	–	–	0.081
unknown	–	–	–	–	–	–	–	0.16
sym. octahydroanthracene	–	0.004	0.018	trace	0.031	0.016	–	–
sym. octahydrophenanthrene	–	0.024	0.057	0.004	0.10	0.072	–	–
tetrahydroanthracene/ tetrahydrophenanthrene	–	0.010	0.052	–	0.14	0.081	–	–
dihydroanthracene/ dihydrophenanthrene	–	0.007	0.024	–	0.083	0.051	–	–
anthracene/ phenanthrene	–	0.010	0.039	–	0.35	0.18	–	–
fluorene	–	–	–	–	–	–	0.13	–

Table 3-22, continued
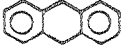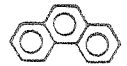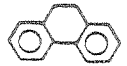
C = Concentration, X = Conversion

Run #	130	232	134	139	112	116	133	132
Substrate	—	(structure)	(structure)	(structure)	(structure)	(structure)	(structure)	(structure)
Products	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%
alkylfluorenes	-	-	-	-	-	-	0.10	-
dihydrodibenzocycloheptene	-	-	-	-	-	-	-	0.16
wt% to tar	0.4	1.5	2.1	1.6	3.0	5.1	2.8	2.0
Substrate to Prodcuts	X,mole%	X,mole%	X,mole%	X,mole%	X,mole%	X,mole%	X,mole%	X,mole%
total	-	99.8	99.5	100	93.5	98.7	96.8	96.4
tetralin	-	5.2	5.4	5.6	2.4	3.6	0.7	-
alkyltetralins/ asym. octahydroanthracene/ asym. octahydrphenanthrene	-	2.7	3.3	2.5	2.1	3.1	0.8	0.1
dihydronaphthalene	-	0.5	0.6	0.6	0.2	0.3	-	-
naphthalene	-	1.7	2.3	2.0	1.5	2.3	-	-

Table 3-22, continued

X = Conversion

Run #	130	232	134	139	112	116	133	132
Substrate	—							
Substrate to Products	X,mole%	X,mole%	X,mole%	X,mole%	X,mole%	X,mole%	X,mole%	X,mole%
{alkylnaphthalenes/ alkyldiphenylalkanes	-	2.1	2.5	1.2	1.9	3.8	15	28
sym. octahydroanthracene	-	0.1	0.4	(trace)	0.5	0.4	-	-
sym. octahydrophenanthrene	-	0.5	1.3	0.1	1.8	1.7	-	-
{tetrahydroanthracene/ tetrahydrophenanthrene	-	0.2	1.2	-	2.4	2.0	-	-
{dihydroanthracene/ dihydrophenanthrene	-	0.2	(0.5)	-	1.5	(1.3)	-	-
{anthracene/ phenanthrene	-	(0.2)	0.9	-	(6.5)	4.5	-	-
fluorene	-	-	-	-	-	-	(3.2)	-
dihydrodibenzycycloheptene	-	-	-	-	-	-	-	(3.6)
alkylfluorenes								
{alkylanthracenes/ alkylphenanthrenes	-	-	0.2	-	2.9	2.2	2.3	-
tar & alkylbenzenes	-	86	81	88	76	77	78	68
(maximum alkylbenzenes)	-	(15)	(31)	(100)	(54)	(49)	(80)	(99)

mixture of phenanthrene reaction due to their high reactivity.

Cracking of the central ring occurred to a substantial degree for both 5 and 7 carbon structures. The resulting alkyldiphenylalkanes, such as methylbiphenyl from fluorene or methylbibenzyl from dihydro-dibenzocycloheptene, reacted further to give diphenylalkanes and alkyl-benzenes. Some cracking of the central ring occurred for 6 carbon structures in dihydroanthracene and dihydrophenanthrene. These occurred to a much lesser extent than cracking of the saturated side rings of tetrahydro and octahydro derivatives.

C. <u>Source of Hydrogen</u>

The experiments in this section were undertaken for the same purpose as those with $ZnCl_2$. The experiments with 1-naphthol and anthracene using $AlCl_3$ catalyst were repeated using nitrogen gas instead of hydrogen. The reaction conditions, product distribution and conversion of substrates to products are presented in Tables 3-23 and 3-24. The results of experiments with the above compounds in which hydrogen gas was used are also presented in these tables for comparison.

Unlike the reactions in the presence of $ZnCl_2$, when $AlCl_3$ was used as catalyst, the substrates were reactive in the absence of hydrogen. The conversions of substrates to products were slightly lower in reactions with nitrogen than those with hydrogen. The conversion of naphthol dropped from 94% to 87%, that of anthracene from 99.8% to 95%. The product distribution of two-ring structures resulting from reaction of naphthol did not depend significantly on the gas used. For anthracene, the conversion of hydrogenated products to two ring structures was suppressed in the absence of hydrogen gas.

Similar experiments were carried out at 225°C using naphthalene

Table 3-23

Source of Hydrogen in Reaction of 1-Naphthol in Cyclohexane
in the Presence of $AlCl_3$

Reaction Conditions: mole% naphthol = 2.0, mole $AlCl_3$/mole
naphthol = 0.54, T = 325°C, P (at 25°C) =
600 psig, P (at T) = 1600 psig, t = 1 hr
at T

Run #	135	233
Gas	Hydrogen	Nitrogen
Products	Concentration (wt%)	Concentration (wt%)
alkanes	0.033	0.035
methylcyclopentane	1.49	0.32
cyclohexane	97.8	98.6
benzene	0.004	0.031
ethylcyclohexane	0.016	-
toluene	0.016	0.043
ethylbenzene	0.004	0.005
o-xylene	0.001	-
methylethylbenzene	0.001	-
butylbenzene	0.015	0.008
diethylbenzene	0.010	0.005
indan	0.005	0.011
methylindans	0.009	0.010
tetralin	0.11	0.094
dihydronaphthalene	0.008	0.005
naphthalene	0.13	0.18
4-methyltetralin	0.002	-
1-methylnaphthalene	0.003	0.052
2-methylnaphthalene	0.002	0.002
ethylnaphthalene	0.006	0.009
higher alkylnaphthalenes	0.011	0.003
tetralone	0.070	0.059
1,2,3,4-tetrahydro-1-naphthol	trace	trace
5,6,7,8-tetrahydro-1-naphthol	0.003	0.004
1-naphthol	0.20	0.47
wt% to tar	-	0.5

Table 3-23, continued

Run #	135	233
Gas	Hydrogen	Nitrogen
Naphthol to Products	Conversion (mole %)	Conversion (mole %)
total	94	87
tetralin	3.4	2.9
alkyltetralins	trace	--
dihydronaphthalene	0.3	0.2
naphthalene	4.2	5.7
alkylnaphthalenes	0.6	0.4
tetralone	2.0	1.6
1,2,3,4-tetrahydro-1-naphthol	trace	trace
5,6,7,8-tetrahydro-1-naphthol	0.1	0.1
tar & alkylbenzenes	84	76
(maximum alkylbenzenes)	(3)	(5)

Table 3-24

Source of Hydrogen in Reaction of Anthracene in
Cyclohexane in the Presence of AlCl₃

Reaction Conditions: mole% anthracene = 2.1, mole AlCl$_3$/mole
anthracene = 0.54, T = 325°C, P (at 25°C) =
600 psig, P (at T) = 1600 psig, t = 1 hr at T

Run #	232	231
Gas	Hydrogen	Nitrogen
Products	Concentration (wt%)	Concentration (wt%)
alkanes	0.39	0.41
methylcyclopentane	6.7	1.3
cyclohexane	91.9	97.5
methylcyclohexane	0.14	0.014
benzene	0.11	0.037
ethylcyclohexane	0.035	trace
toluene	0.063	0.035
ethylbenzene	0.064	0.022
o-xylene	0.010	0.003
propylbenzene	0.019	0.006
trimethylbenzene	0.010	0.003
diethylbenzene	0.033	0.006
indan	0.033	0.003
indene	0.020	–
methylindans	0.043	0.003
tetralin	0.17	0.046
dihydronaphthalene	0.017	0.003
1-methyltetralin	0.041	0.005
naphthalene	0.055	0.050
5-methyltetralin	0.010	–
ethyltetralin	0.026	–
1-methylnaphthalene	0.016	0.014
2-methylnaphthalene	0.010	0.003
phenylcyclohexylethane	0.009	–
biphenyl/ethylnaphthalene	0.032	0.004
diphenylmethane/butyltetralin	0.007	0.002

Table 3-24, continued

Run #	232	231
Gas	Hydrogen	Nitrogen
Products	Concentration (wt%)	Concentration (wt%)
butyldihydronaphthalene/ asym. octahydroanthracene/ asym. octahydrophenanthrene/ bibenzyl	0.024	0.021
butylnaphthalene	0.004	–
sym. octahydroanthracene	0.004	0.003
sym. octahydrophenanthrene	0.024	0.034
tetrahydroanthracene	0.010	0.25
dihydroanthracene	0.007	0.030
anthracene	0.010	0.23
alkylanthracenes	–	0.011
wt% to tar	1.5	2.4

Table 3-24, continued

Run #	232	231
Gas	Hydrogen	Nitrogen
Anthracene to Products	Conversion (mole%)	Conversion (mole%)
total	99.8	95
tetralin	5.2	1.3
dihydronaphthalene	0.5	0.1
alkyltetralins/ asym. octahydroanthracene/ asym. octahydrophenanthrene	2.	0.6
naphthalene	1.7	1.5
alkylnaphthalenes/ alkyldiphenylalkanes	1.9	0.6
sym. octahydroanthracene	0.1	0.1
sym. octahydrophenanthrene	0.5	0.7
tetrahydroanthracene	0.2	5.3
dihydroanthracene	0.2	0.6
alkylanthracenes	-	0.2
tar & alkylbenzenes	86	84
(maximum alkylbenzenes)	(15)	(5)

as the substrate. The results were presented in Table 3-13 and discussed in section I-C. The product distribution of naphthalene products was independent of whether hydrogen or nitrogen atmospheres were used. These results indicated that the hydrogen used in the hydrogenation reaction of substrates in the presence of $AlCl_3$ catalyst may have come from Scholl condensation of the substrate as well as the atmospheric hydrogen. Similar results have been obtained for anthracene in the presence of $SbCl_3$, in which Scholl condensation of anthracene provided the hydrogen necessary for anthracene hydrogenation (54).

It is interesting to note that the concentration of alkylbenzenes in the product mixture dropped for reactions of anthracene and naphthol when nitrogen gas was used instead of hydrogen. This could indicate that the conversion of substrates to alkylbenzenes was reduced in the absence of hydrogen gas. This hypothesis may be supported by the observation that for the reactions of naphthol and anthracene, the amount of tar recovered increased when nitrogen gas was used but conversion of substrate to tar plus alkylbenzenes remained relatively constant. However, it is also observed that concentration of methylcyclopentane was lower when nitrogen gas was used than when hydrogen was used. This could indicate that the lower concentration of alkylbenzenes when nitrogen gas was used was due to lower reaction rate of cyclohexane. This in turn could indicate that the cyclohexane solvent had an effect in providing hydrogen for reaction of substrates in the presence of $AlCl_3$.

IV. Diagnostic Experiments

These experiments were carried out to determine what sources other than $ZnCl_2$ and $AlCl_3$ could be acting as catalysts in the reactions of

the substrates. The reactions were carried out using anthracene as the substrate and reaction conditions similar to those of the substrate reactivity experiments. The reaction conditions and results of these reactions are presented in Table 3-25. The results of the reactions of anthracene in the substrate reactivity experiments in the presence of $ZnCl_2$ and $AlCl_3$ are also presented in this table.

An experiment was carried out in the absence of the catalysts. The conversion was reduced to 44%, mostly to dihydroanthracene. This is 2/3 of the value observed in the presence of the weaker catalyst, $ZnCl_2$. The sources of catalyst in this case may have been the surface of the glass liner or the metal in contact with the reaction mixture, namely the stirring shaft and propeller. An experiment was carried out without the glass liner. The conversion was reduced to 20%. Thus both the glass liner and the stirring shaft were sources of catalysts.

In the next experiment a base was added to the reaction mixture to determine whether the hydrogenation of anthracene, in the absence of $ZnCl_2$ or $AlCl_3$, was purely a thermal reaction or if the acidic sites on the glass and metal surfaces acted as catalyst. Addition of NaOH pellets had no effect on the reaction, due to insolubility of sodium hydroxide in the reaction medium. When pyridine was added to the reaction mixture, conversion of anthracene to hydrogenated products was reduced to 8%. Pyridine itself did not react under these reaction conditions. So, this indicated that the effective catalyst in the absence of $ZnCl_2$ or $AlCl_3$ was the acidic sites on the glass surface or the metal halides formed on the surface of the stirring shaft.

V. Reaction Mechanisms

In this section, possible reaction sequences are proposed for

Table 3-25

Catalyst Sources in Reactions of Anthracene in Cyclohexane

Reaction Conditions: mole% anthracene = 2.0-2.2, mole catalyst/mole anthracene = 0.54,
T = 325°C, P (H$_2$, at 25°C) = 600 psig, P (at T) = 1600 psig,
t = 1 hr at T

C = Concentration

Run #	232	47	257	257-3	257-1	257-2*
Catalyst	AlCl$_3$	ZnCl$_2$	-	-	-	-
Conditions/Additives	-	-	-	no glass liner	dry NaOH	Pyridine 3.7 mole%
Products	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%
alkanes	0.39	-	-	-	-	-
methylcyclopentane	6.7	-	-	-	-	-
cyclohexane	91.9	96.7	97.8	98.6	97.7	99.3
alkylbenzenes	0.44	trace	-	-	-	-
tetralin	0.17	-	-	-	-	-
dihydronaphthalene	0.017	-	-	-	-	-
alkyltetralins	0.11	-	-	-	-	-
naphthalene	0.055	-	-	-	-	-
alkylnaphthalenes	0.071	0.023	0.005	0.002	trace	-
sym. octahydroanthracene	0.028	0.12	0.028	0.011	0.010	-
tetrahydroanthracene	0.010	0.57	0.41	0.14	0.40	-
dihydroanthracene	0.007	2.27	1.53	0.78	1.60	0.37
anthracene	0.010	0.31	0.28	0.40	0.25	0.31

Table 3-25, continued

X = Conversion

| Run #	232	147	257	257-3	257-1	257-2*
Catalyst	$AlCl_3$	$ZnCl_2$	–	–	–	–
Conditions/Additives	–	–	–	no glass liner	dry NaOH	Pyridine 3.7 mole%
Anthracene to Products	X,mole%	X,mole%	X,mole%	X,mole%	X,mole%	X,mole%
total, liquid	13-29	68	44	21	45	8.2
alkylbenzenes	max 16	trace	–	–	–	–
alkylnaphthalenes + dihydronaphthalene + tetralin	3.4	0.5	0.1	trace	–	–
octahydroanthracene	0.6	3.2	0.6	0.2	0.2	–
tetrahydroanthracene	0.2	13	9.2	3.2	8.9	–
dihydroanthracene	0.2	51	35	18	36	8.2
precipitation/ polymerization	71-87	25	47	67	49	85

*The concentration values given for products do not include pyridine.

hydrogenation and cracking of the substrates studied in the presence

of $ZnCl_2$ and $AlCl_3$. In most instances, evidence for these sequences

is drawn from the results obtained using $ZnCl_2$ since relative substrate

reactivities are more clearly evident in this case. The results of

reactions in the presence of $AlCl_3$ are used as evidence for inter-

mediate and final stages of hydrogenolysis. Mechanisms proposed to

explain the results of the present investigation are compared to those

previously presented in the literature, where available.

Prior to examining detailed reaction mechanisms, it is important

to know the exact form of the catalyst. It has been observed that $AlCl_3$

does not initiate many Friedel-Crafts reactions unless a complexing

agent such as water or HCl is present (61,65). It has been suggested

that hydrogen chloride, formed by the reaction of water with $AlCl_3$,

could serve to activate the catalyst. There has also been experimental

evidence to show that water itself can activate $AlCl_3$ (65). The

activity of $ZnCl_2$ is also enhanced by the presence of water (49,66).

Since the present work was not carried out under completely anhydrous

conditions, it is likely that the active catalyst species were as

follows: $H^+(ZnCl_2OH)^-$ (7), and $H^+(AlCl_3OH)^-$ or $H^+(AlCl_4)^-$ (61,65). The

active species are all Brönsted acids and are known to participate in

reactions in a manner similar to other proton acids (67).

It is well established that carbonium ions are formed in the

presence of strong acids (68). Indications of this have been given

based on quantum mechanical calculations and NMR spectroscopy observa-

tions (69, 70, 71). Recently, the formation of carbonium ions of the

types 1, 2, and 3 in the presence of superacids has been confirmed by

Olah and his coworkers using ^{13}C NMR (72,73). Carbonium ions
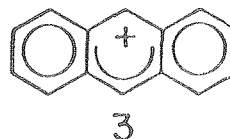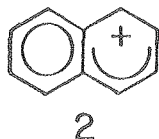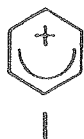
of this type occur as intermediates in a number of electrophilic

reactions (68).

The reaction mechanisms proposed in the present work are explained

on the basis of carbonium ion intermediates. For example, naphthalene

is protonated in the presence of AlCl$_3$ to form the naphthalenium ion.

The resulting complex is most likely in the form of an ion pair rather

than free ions, since the low dielectric strength of cyclohexane should

preclude the existence of a substantial number of free ions. However,

in this section the protonation step will be designated in the following

form for simplicity.

A. Hydrogenation and Cracking of Naphthalene

A possible reaction sequence for naphthalene hydrogenation and

cracking, based on products observed in reactions of naphthalene, di-

hydronaphthalene and tetralin in the presence of ZnCl$_2$ and AlCl$_3$

catalysts, is presented in Fig. 3-1. This sequence involves stepwise

hydrogenation of naphthalene to dihydronaphthalene and tetralin,
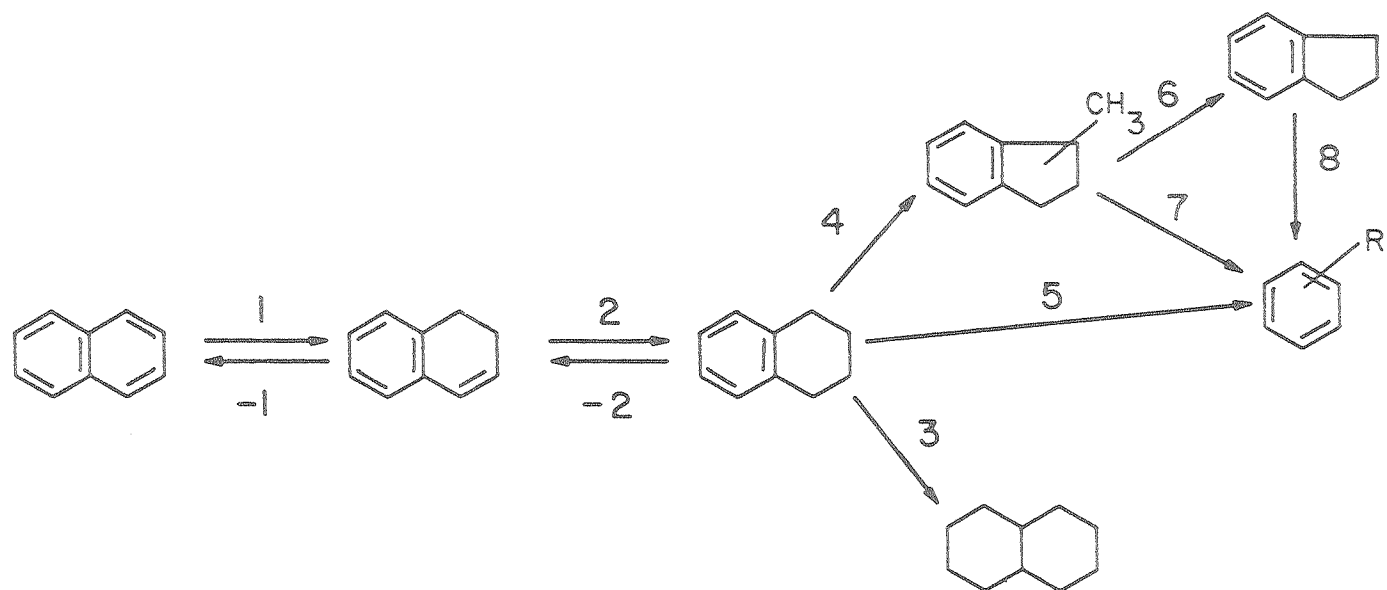
Fig. 3-1. Hydrogenation and Cracking of Naphthalene

XBL 803-8956

followed by further hydrogenation of tetralin to decalin, or cracking of
tetralin to form alkylbenzenes. The last step may occur directly, or
through methylindan and indan intermediates. In this reaction mechanism,
represents benzene as well as mono-, di- and tri-substituted
alkylbenzenes. The same notation will be used in other reaction
mechanisms appearing in the present work. Reaction sequences similar
to that given in Fig. 3-1 have been proposed for hydrogenation and
cracking of naphthalene in the presence of solid acid catalysts (74) and
the strong acid catalyst HF/TF_5 (75).

The reaction of naphthalene in the presence of $ZnCl_2$ at 325°C and
1600 psig (Table 3-16) was slow, with 0.5% conversion to tetralin and less
than 0.1% conversion to dihydronaphthalene. This indicates that the
rate of the reaction through path 1, r_1, is low. Under the same reaction
conditions, dihydronaphthalene was quite reactive with 61% conversion to
tetralin and 19% conversion to naphthalene. This indicates that
hydrogenation of naphthalene to dihydronaphthalene is slower than the
reverse reaction ($r_1 < r_{-1}$). However, hydrogenation of dihydronaphthalene
occurs more rapidly than dehydrogenation, as evidenced by the conversion
values to tetralin and naphthalene ($r_2 > r_{-1}$). Thus, tetralin is formed
as a result of this reaction sequence. Tetralin was not very reactive
under these reaction conditions, giving small conversions to decalin,
methylindan, indan, alkylbenzenes and naphthalene. This indicates that
reaction rates r_{-2}, r_3, r_4, r_5, etc., are relatively low. Cracking and
isomerization-cracking of tetralin involves a complex series of
reactions (75). Steps 4-8 in Fig. 3-1 are a simplification of such a
reaction series based on products observed in reactions of naphthalene,
dihydronaphthalene and tetralin in the present work. The relative rates
of these steps are not known. Due to the small conversion of tetralin

to decalin, methylindan, indan and alkylbenzenes, it is not possible to compare the rate of cracking with the rate of hydrogenation of tetralin based on results of the present work. However, in a similar reaction sequence proposed for naphthalene in the presence of strong acid catalysts (75), conversion of tetralin to decalin was low. In reaction of naphthalene in the presence of $ZnCl_2$ under more severe reaction conditions, alkylbenzenes were the final products rather than decalin (see Table 1-1). Thus, it may be concluded that r_4, $r_5 > r_3$.

The products observed in reactions of naphthalene and tetralin in the presence of $AlCl_3$ at 225°C and 1000-1600 psig (Tables 3-6, 3-7, 3-8 and 3-11), were similar to those observed in reactions in the presence of $ZnCl_2$. The same held true for reactions of naphthalene, dihydro-naphthalene and tetralin in the presence of $AlCl_3$ at 325°C and 1600 psig (Table 3-21). The higher conversions observed in these cases indicate that the reaction rates are higher in the presence of the stronger acid, $AlCl_3$. The rates of polymerization of naphthalene, polymerization of aromatic reaction intermediates and copolymerization of naphthalene and aromatic reaction intermediates are also high in the presence of $AlCl_3$, as evidenced by high conversions of naphthalene, tetralin and dihydro-naphthalene to tar.

The proposed reaction sequence can be explained based on carbonium ion intermediates. Naphthalene is protonated in the first step of the reaction (75, 76, 77).

(I)
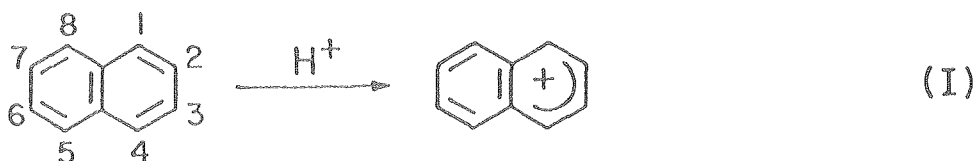
The 1-position is more reactive than 2-position for protonation because the resulting carbonium ion has better resonance stabilization (78). As explained by Streitwieser and Heathcock (78), when protonation occurs in 1-position, the charge can be distributed in five different positions.
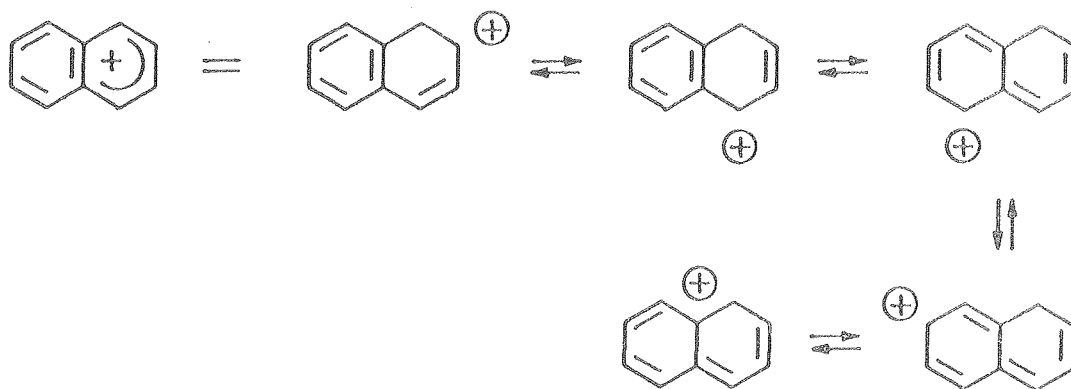
The first two structures have an intact benzene ring and are thus more stable than the remaining three structures. The first two structures contribute much more to the overall resonance hybrid. When protonation occurs at the 2-position, the charge is also distributed in five different positions, but only one structure has an intact benzene ring. The resulting resonance hybrid in the latter case has higher energy than the former case, in which protonation occurs at the 1-position. Thus, protonation occurs mostly at the 1-position.

The preference for protonation at the 1-position can also be explained based on basicity of this s e. Brouwer, et al. (68) have measured basicity constants K_B, for formation of carbonium ions from arenes in liquid hydrofluoric acid. For reaction of compound A,

$$A + 2\ HF \rightleftharpoons AH^+ + HF_2^-$$

the basicity constant for a protonation site, $(K_B)_i$, is defined as:

$$(K_B)_i = (m_{AH^+} \, m_{HF_2^-}/m_A)(f_{\pm}^2/f_A)$$

where m_{AH^+}, m_{HF^-}, and m_A are the molalities of the carbonium ion, the fluoride ion and the unprotonated arene respectively and $f_{\pm}$ and f_A are the activity coefficients. The total basicity constant, K_B is defined as

$$K_B = \sum_i \nu_i (K_B)_i$$

where ν_i is the number of equivalent sites due to symmetry. The measured basicities are closely correlated with reactivities of the respective sites in electrophilic substitution reactions. For naphthalene, $\log (K_B)_1 = -4.6$, whereas $\log(K_B)_2 = -6.4$. This also indicates that the 1-position is the more reactive site for protonation.

The carbonium ion formed upon protonation of naphthalene, reaction 1, can subsequently react with a hydride source to form dihydronaphthalene,

(II)
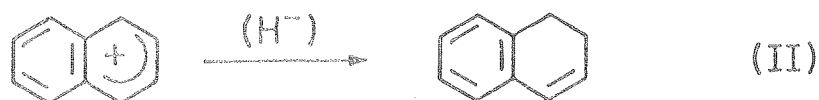
or a molecule of naphthalene to form binaphthyl and other products of Scholl condensation (64, 79).

(III)
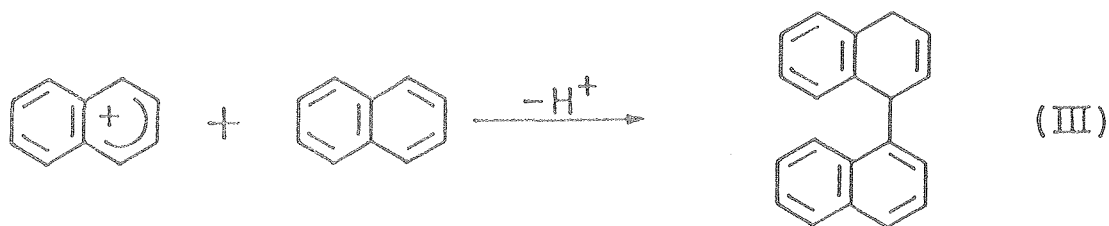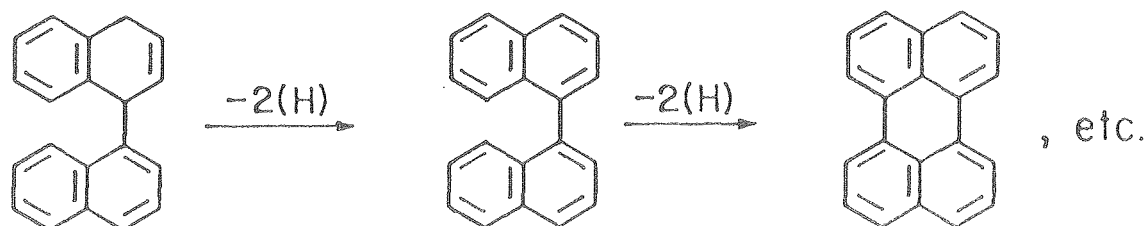
The occurrence of the latter process is undesirable since it leads to the formation of high molecular weight products and tar. The extent to which Scholl condensation takes place depends on the strength of the catalyst and the basicity of aromatic substances present in solution. The Brönsted acid form of a strong Lewis acid such as $AlCl_3$ is more acidic than that for a weaker Lewis acid such as $ZnCl_2$. As a consequence, it is expected that the concentration of protonated naphthalene species is higher in the presence of $AlCl_3$. Furthermore, it is expected that the extent of charge transfer is greater for the anion/cation pair formed from naphthalene and the Brönsted acid form of $AlCl_3$ than from naphthalene and the Brönsted acid form of $ZnCl_2$. Both of these factors enhance the rate at which Scholl condensation occurs (79).

The hydride ion required to form dihydronaphthalene can come from two sources. The first is hydride transfer from a hydrocarbon species. One source for such ions is the initial product formed during Scholl condensation (54). The results presented in Tables 3-13, 3-23 and 3-24 clearly demonstrate that this was the primary source of hydride ions when $AlCl_3$ was used as the catalyst. Methylcyclopentane formed by isomerization of cyclohexane in the presence of $AlCl_3$ may also serve as a tertiary hydride donor (75, 80), in the manner shown below.

$$\text{(reaction scheme)} \qquad (IV)$$

$$\text{(reaction scheme)}$$
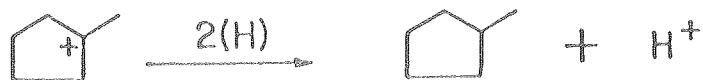
However, in the present work this mechanism did not seem to be operative, since the addition of methylcyclopentane to the reactants for reaction of naphthalene in the presence of $AlCl_3$ did not affect the products formed (see section I-C). The second source of hydride ions is the heterolytic dissociation of H_2.

$$\text{(reaction scheme)} \qquad (V)$$

The results presented in Tables 3-18 and 3-19 suggest that this was the primary source of hydride ions when $ZnCl_2$ was used. Presumably dissociation is affected by coordination of molecular hydrogen to the cation/anion pair.

Protonation and hydride abstraction of dihydronaphthalene to form tetralin, step 2 of the reaction sequence in Fig. 3-1, involves reaction paths similar to those discussed for naphthalene.

$$\text{(reaction scheme)} \qquad (VI)$$
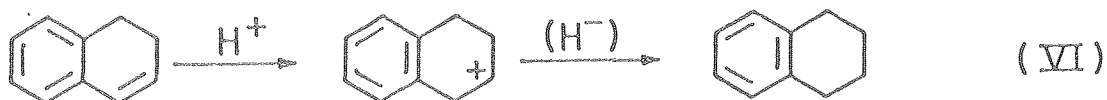
Dihydronaphthalene may also be dehydrogenated by reverse of reactions II and I and act as source of hydride or proton or add to other molecules in the process of Scholl condensation.

Tetralin can react to form decalin by a series of protonations and hydride abstractions, in a fashion analogous to the hydrogenation of naphthalene to form tetralin.

$$\text{(VII)}$$
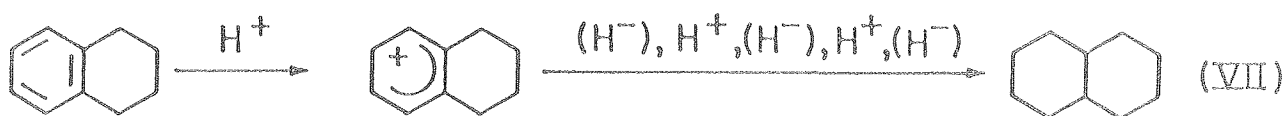
The rate of reaction VII is low in the presence of acid catalysts (75). The more favored path involves a complex series of reactions to form alkylbenzenes (75). A simplification of such paths may be represented by the following sequence:

$$\text{(VIII)}$$
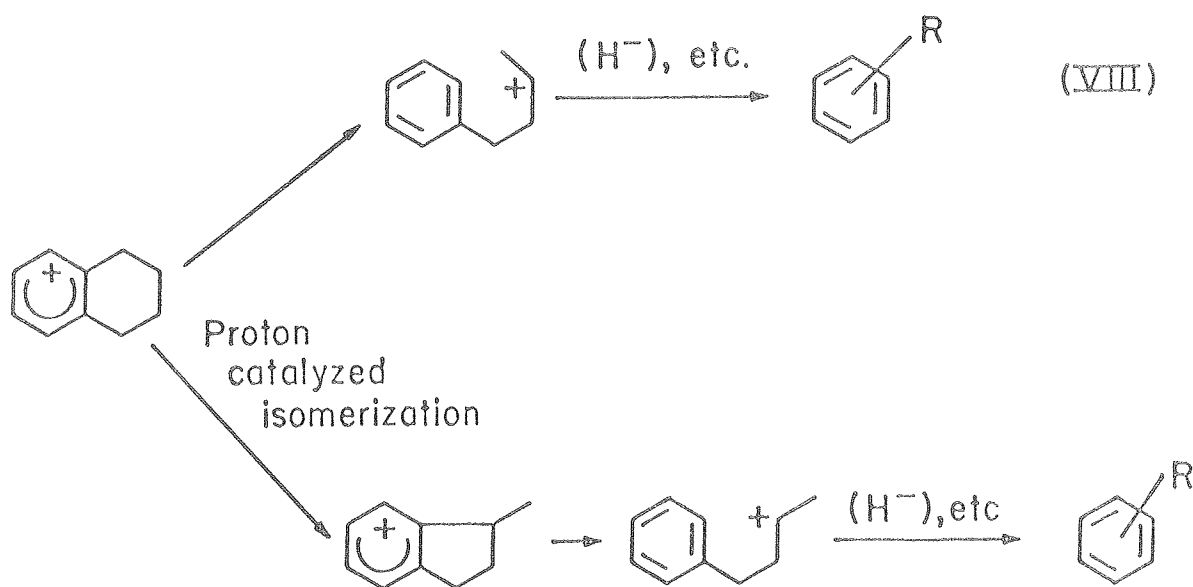
B. Hydrogenation and Cracking of 1-Methylnaphthalene

A possible reaction sequence for hydrogenation and cracking of
1-methylnaphthalene based on products observed during its reactions in
the presence of $ZnCl_2$ and $AlCl_3$ is presented in Fig. 3-2. In this
reaction sequence, disproportionation of 1-methylnaphthalene results in
formation of naphthalene, step 1, which hydrogenates further by the
reaction sequence discussed in the previous section. Hydrogenation of
either ring occurs, forming 5-methyltetralin, step 2, and 1-methyl-
tetralin, step 3. The two methyltetralins undergo cracking to form
alkylbenzenes, steps 7 and 8, or disproportionation to form tetralin,
step 5.

The reaction of 1-methylnaphthalene at 325°C and 1600 psig in the
presence of $ZnCl_2$ was faster than that of naphthalene, as indicated by
6% conversion of 1-methylnaphthalene to products, compared to 0.6% for
naphthalene (Table 3-16). This can be explained by the higher basicity
of 1-methylnaphthalene. Log K_B, defined in the previous section, is -1.7
for 1-methylnaphthalene, compared to the value of -4.0 for naphthalene
(68). Conversions of 1-methylnaphthalene to naphthalene and higher
alkylnaphthalenes were both 0.2%. This indicates that formation of
naphthalene was due to disproportionation of 1-methylnaphthalene.
Conversions of 3.6% to alkyltetralins and 1.1% to tetralin indicate that
the rate of disproportionation of 1-methylnaphthalene is lower than
hydrogenation or that r_2, $r_3 > r_1$. Since, as was explained in the
previous section, r_4 is low, tetralin is formed mostly by dispropor-
tionation of alkyltetralins, or, $r_5 > r_4$. Of the 3.6% conversion to
alkyltetralins, 2.6% was to 1-methyltetralin and 1% to dimethyltetralin.
Based on these results, $r_3 > r_2$ unless complete disproportionation of
5-methyltetralin to tetralin and dimethyltetralin was possible under the
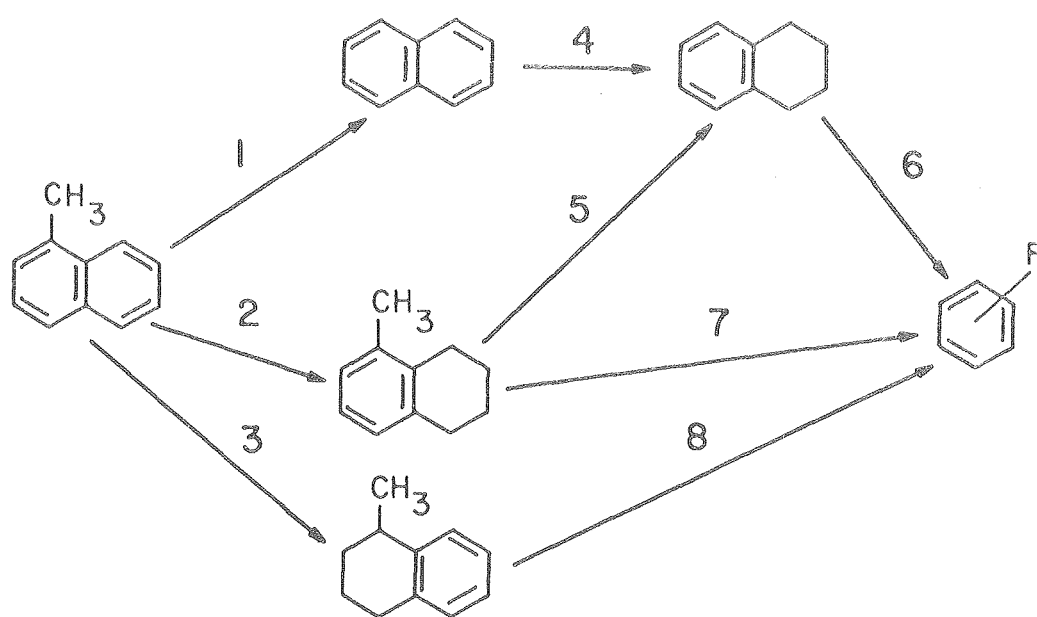
Fig. 3-2. Hydrogenation and Cracking of 1-Methylnaphthalene

XBL 803-8957

present reaction conditions. The results did not provide conclusive evidence for comparison of rates in this case. Considering the small amount of tetralin present in the products and that step 6 is slow, the alkylbenzenes observed in the products were most likely produced via steps 7 and 8, or in other words, r_7, $r_8 > r_6$.

The total conversion of 1-methylnaphthalene to products in the presence of $AlCl_3$ was higher than that of naphthalene (Table 3-21). The observed products included equal amounts of 1-methyltetralin and 5-methyltetralin. The reaction sequence proposed in Fig. 3-2 and the discussion holds true for the observations made in this case, as well.

The proposed reaction sequence may be explained on the basis of carbonium ion intermediates. In the first step, 1-methylnaphthalene is protonated. The protonation is most likely to occur at the 4-position (68).

(I)
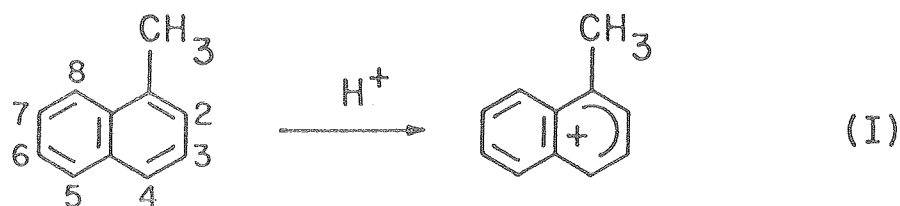
The resulting carbonium ion may abstract a hydride ion and hydrogenate further to form 1-methyltetralin.

(II)
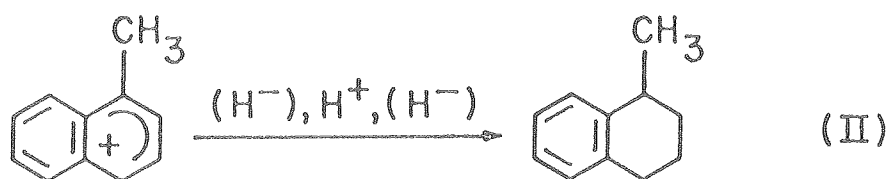
It may also form naphthalene by transferring the methyl carbonium ion to another molecule of 1-methylnaphthalene, most likely to the 4-position (68, 81).

$$(III)$$
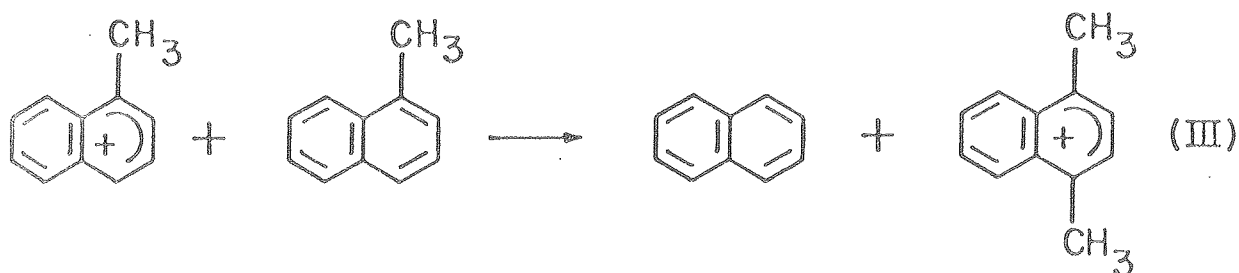
The methyl carbonium ion may also add to other aromatic molecules. The resulting carbonium ion may lose a proton or undergo hydride abstraction and further hydrogenation. For the case when the methyl carbonium ion is added to the 4-position of 1-methylnaphthalene, these paths may be represented as

$$(IV)$$

and

$$(V)$$
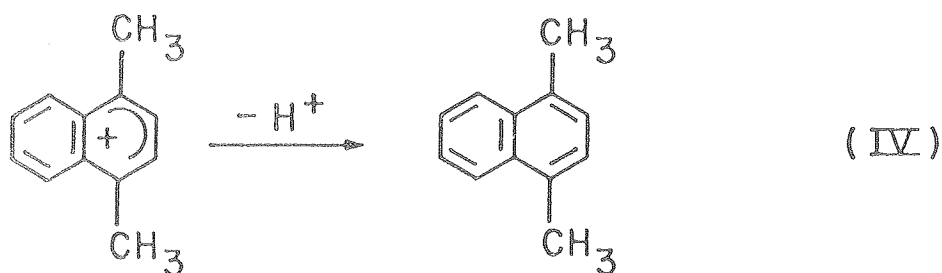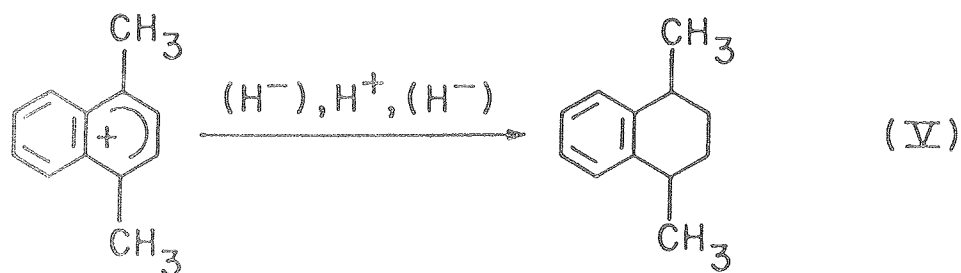
Protonation may also occur at the 8-position of 1-methylnaphthalene, resulting in 5-methyltetralin as the final product.

$$(VI)$$
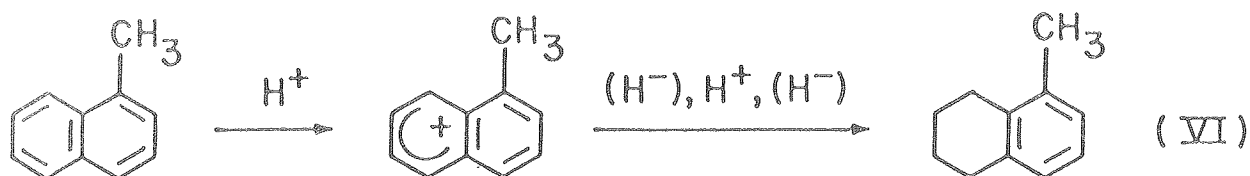
5-methyltetralin may in turn undergo disproportionation to form

tetralin in a manner similar to 1-methylnaphthalene.

(VII)
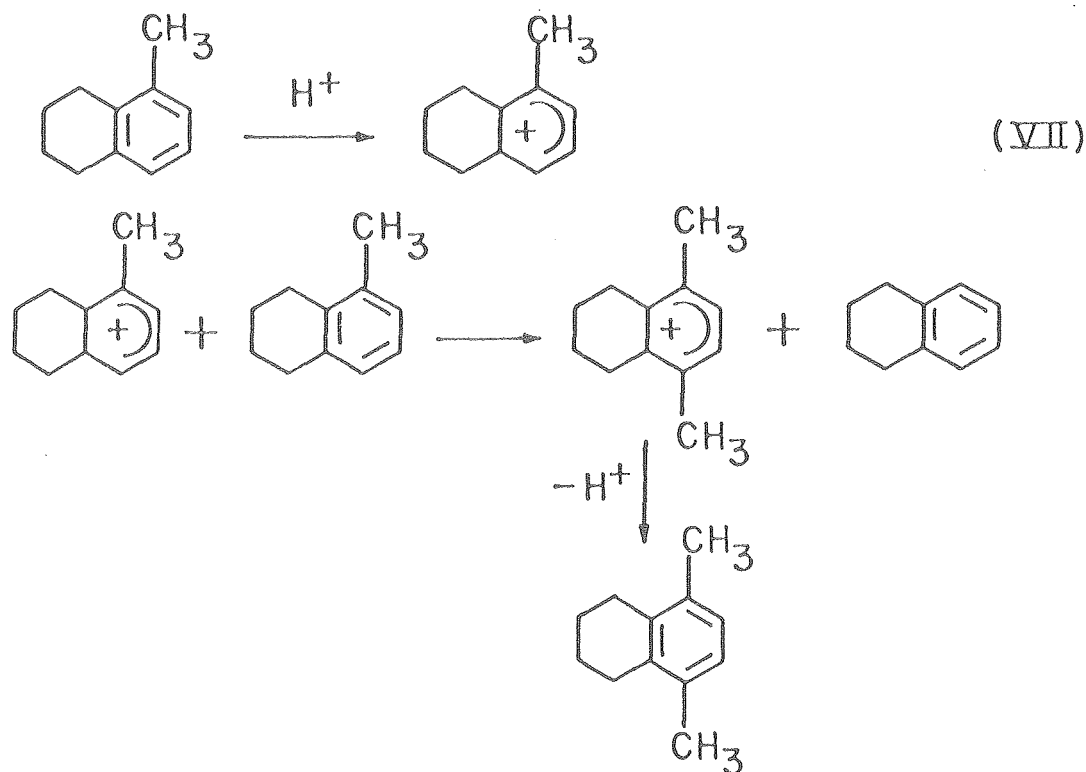
The cracking and polymerization of 1-methylnaphthalene proceed along

steps similar to those discussed previously for naphthalene.

C. Hydrogenation and Cracking of 1-Naphthol

A possible reaction sequence for the hydrogenation and cracking of

1-naphthol, based on the products of reactions of 1-naphthol, 1,2,3,4-

tetrahydro-1-naphthol and 5,6,7,8-tetrahydro-1-naphthol in the presence

of $ZnCl_2$ and $AlCl_3$ is presented in Fig. 3-3. This reaction sequence

involves hydrogenation of both rings of 1-naphthol to form 1,2,3,4-

tetrahydro-1-naphthol (steps 2 and 3) and 5,6,7,8-tetrahydro-1-naphthol

(step 1). This is followed by dehydroxylation and cracking of the

above compounds.

Fig. 3-3. Hydrogenation and Cracking of 1-Naphthol

XBL 803-8955
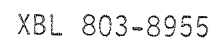
The reaction of 1-naphthol at 325°C and 1600 psig in the presence of $ZnCl_2$ was much faster than that of naphthalene, as indicated by 25% conversion of 1-naphthol to products compared to 0.6% for naphthalene (Tables 3-16). This is due to the strong electron-releasing property of the -OH group which raises the basicity of the aromatic compound substantially (68). Conversions to the hydrogenated naphthol products were 2.1% to 5,6,7,8-tetrahydro-1-naphthol, 3.5% to 1-tetralone, and 0.1% to 1,2,3,4,-tetrahydro-1-naphthol. Conversions to other products were 2.1% to dihydronaphthalene, 14% to tetralin, 3.4% to naphthalene and 0.1% to alkylbenzenes. Under the same reaction conditions, 5,6,7,8-tetrahydro-1-naphthol gave conversions of 1.3% to alkylbenzenes, 0.5% to decalin and 0.4% to tetralin. The above product distributions indicate that tetralin, naphthalene and dihydronaphthalene products observed in reactions of 1-naphthol resulted mostly from reaction through step 2 and not step 1. The conversions of 1,2,3,4 -tetrahydro-1-naphthol to products under the above reaction conditions were 60% to tetralin, 0.5% to dihydronaphthalene and 12% to naphthalene. These results indicate that tetralin and naphthalene did in fact result from reactions through step 2 and the subsequent steps. Relative reaction rates based on the above conversion values are r_2, $r_3 > r_1$ and r_4, r_5, $r_6 > r_{-7}$. The conversions to alkylbenzenes and decalin observed during the reaction of 5,6,7,8-tetrahydro-1-naphthol were higher than could be obtained by reaction of tetralin (see section A). Thus, these compounds were produced by reaction of 1-naphthol via paths 1, 10 and 1, 12, 14. Relative reaction rates based on the above conversion values are $r_{10} > r_8$ and r_{12}, $r_{14} > r_9$. The higher reaction rate for step 2 compared to step 1 is due to the fact that the -OH group increases the reactivity of the ring to which it is attached more than the reactivity of the adjoining ring (68, 81).

The reaction of 1-naphthol in the presence of $AlCl_3$ at 325°C and 1600 psig (Table 3-21) produced conversions to products of 2.0% to tetralone, 4.2% to naphthalene, 3.4% to tetralin and 0.3% to dihydro-naphthalene. Small amounts of the two tetrahydronaphthols were observed in the products. In reaction of 5,6,7,8-tetrahydro-1-naphthol under the same reaction conditions, conversions to products were 4% to decalin, 15% to tetralin, and 3.4% to naphthalene. Alkylphenols and phenol were also observed in the products. Reaction of 1,2,3,4-tetrahydro-1-naphthol produced conversions of 55% to tetralin and 15% to naphthalene. These results indicate that reaction via steps 1, 11, 12, 13 and 14 occurred more rapidly in the presence of $AlCl_3$ than in the presence of $ZnCl_2$. The small amount of alkylbenzenes recovered, 3-4%, during the reactions of the above compounds, indicates that reactions were suppressed once naphthalene and tetralin were formed. As mentioned in Chapter 3, section III-A, this may have been due to deactivation of $AlCl_3$ by the water released in the formation of naphthalene and tetralin.

In the work of Morita, et al. (47), reaction of 2-naphthol at 425°C and 3400 psig resulted in conversions to products of 43% to tetralin, 21% to naphthalene, 7% to methylindan and 22% to benzene and alkylbenzenes (see Table 1-1). These results are also in agreement with the reaction sequence proposed in Fig. 3-3.

The proposed reaction sequence can be interpreted in terms of the reactions of carbonium ion intermediates. Protonation of either ring of 1-naphthol occurs in a fashion similar to that proposed for naphthalene and 1-methylnaphthalene. The intermediate carbonium ions

have better resonance stabilization due to the presence of the -OH group. Hydrogenation of the ring with the -OH group results in the formation of 1-tetralone through an enol-keto equilibrium reaction (81).
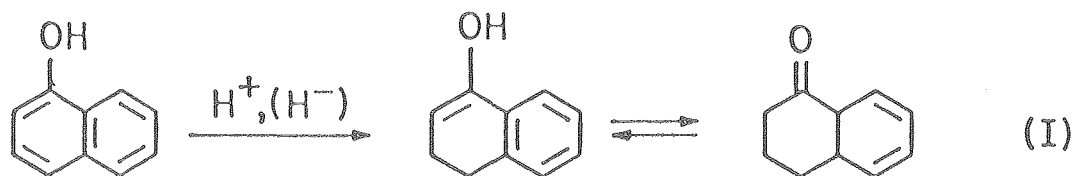
This is followed by further hydrogenation to form 1,2,3,4-tetrahydro-1-naphthol.
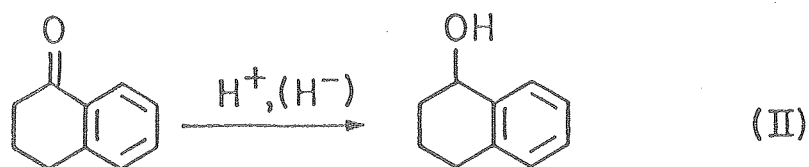
Protonation of the oxygen in 1,2,3,4-tetrahydro-1-naphthol results in formation of tetralenium ion which can abstract a hydride to form tetralin or lose a proton to form dihydronaphthalene.
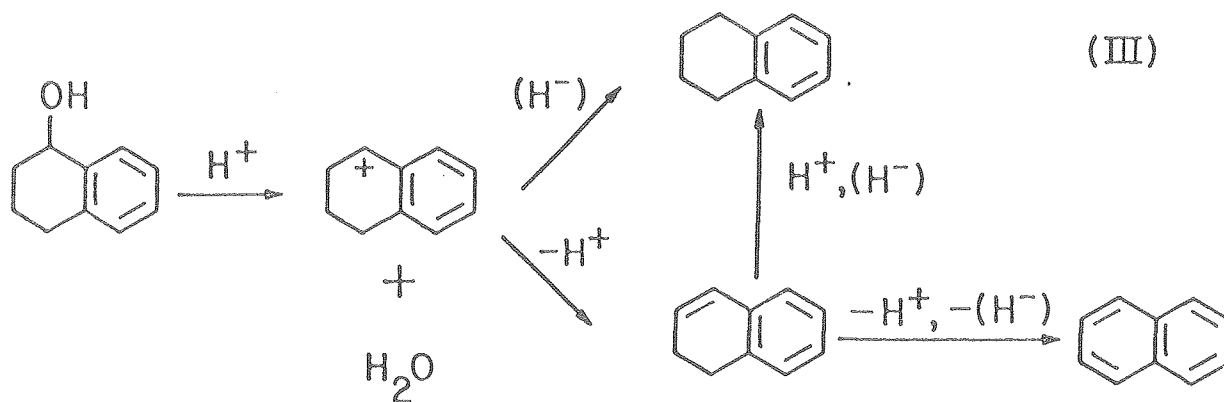
Dihydronaphthalene, in turn, hydrogenates to form tetralin or de-hydrogenates to form naphthalene, as discussed in section A.

The conversion of 5,6,7,8-tetrahydro-1-naphthol to decalin, step 10, is similar to conversion of 1-naphthol to 1,2,3,4-tetrahydro-1-

naphthol, and proceeds by a similar mechanism. Cracking of the saturated ring of 5,6,7,8-tetrahydro-1-naphthol resembles the cracking of tetralin, but occurs to a larger extent because of the presence of the electron releasing -OH group. Substituent removal or disproportionation of the resulting alkylphenol results in formation of phenol or alkylnaphthalenes.

D. Hydrogenation and Cracking of Anthracene

A possible reaction sequence for anthracene hydrogenation and cracking, based on products of reactions of anthracene, dihydroanthracene and octahydroanthracene in the presence of $ZnCl_2$ and $AlCl_3$ is presented in Fig. 3-4. This sequence involves hydrogenation of anthracene to form dihydroanthracene and tetrahydroanthracene, which hydrogenate further to produce octahydroanthracenes. These reactions are followed by cracking to form alkylnaphthalenes and alkyltetralins, which proceed to react in the manner discussed previously. Similar mechanisms involving hydrogenation, isomerization and cracking have been proposed for reaction of anthracene using solid acid catalysts (76) and $ZnCl_2$ at 400°C and 3400 psig (51). The above investigators have proposed that the cracking of saturated side rings of tetrahydroanthracene and sym -octahydroanthracene proceed through an initial isomerization of the following type prior to the occurrence of cracking.

$$(I)$$
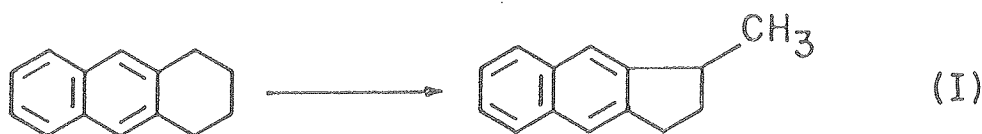
There was no evidence in the results of the present work to support the above suggestion. This is perhaps due to overlapping of the GC peaks
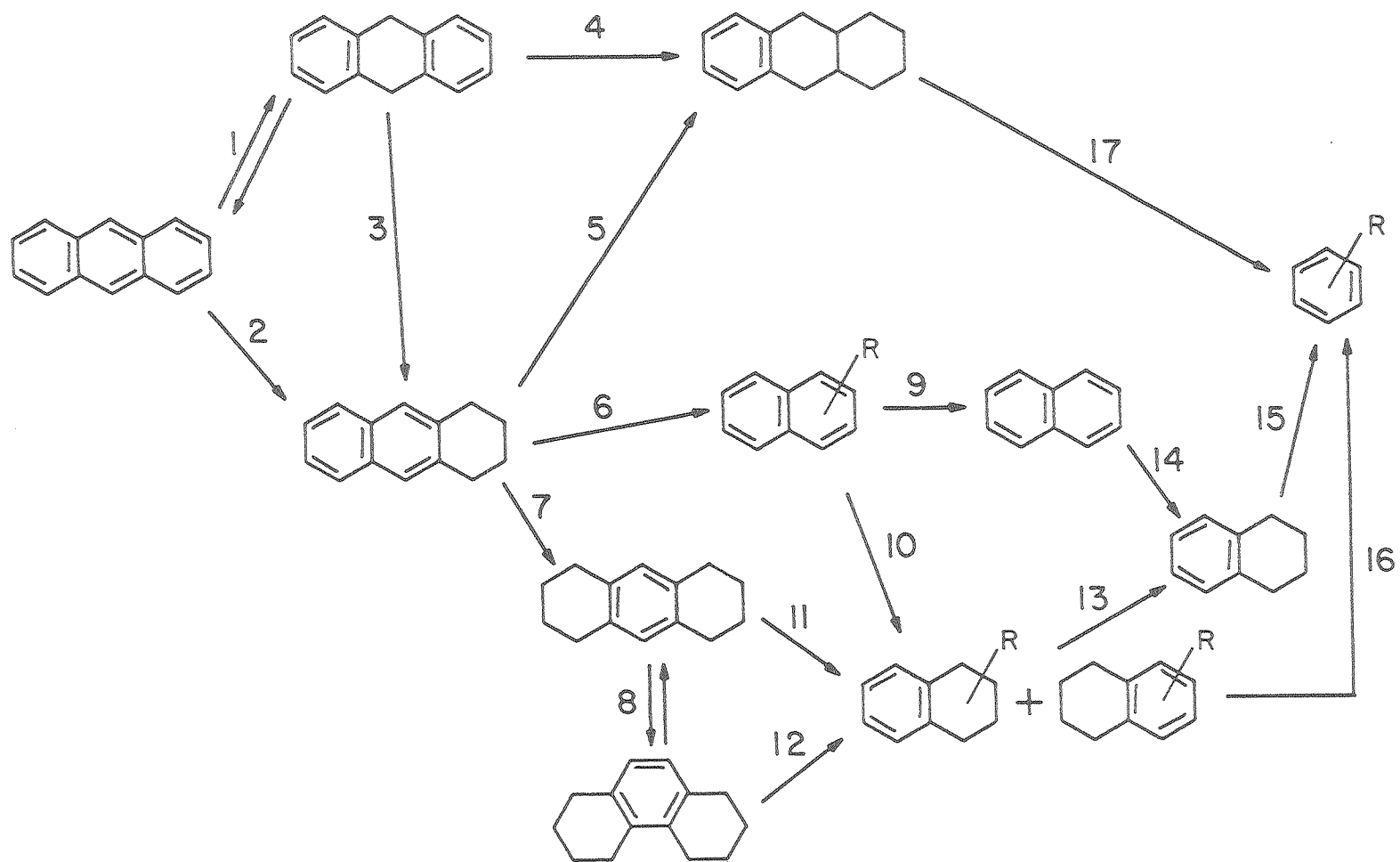
Fig. 3-4. Hydrogenation and Cracking of Anthracene

XBL 803-8952

of tetrahydroanthracene and its isomer of the above type and the over-
lapping of the GC peaks of sym -octahydroanthracene and its isomer of
the above type.

The reaction of anthracene at 325°C and 1600 psig in the presence
of $ZnCl_2$ was much faster than that of naphthalene, as indicated by 68%
conversion of anthracene to products compared to 0.6% conversion of
naphthalene (Tables 3-16 and 3-17). This may be explained by the much
higher basicity of anthracene. Log K_B, defined in section V-A, is 3.8
for anthracene compared to -4.0 for naphthalene (68). Conversion of
anthracene to 9,10-dihydroanthracene, step 1, was rapid. In the
presence of $ZnCl_2$ at 325°C and 1600 psig (Table 3-17), conversions of
anthracene to dihydroanthracene and tetrahydroanthracene were 51% and
13% respectively. The above results indicate that $r_1 > r_2$. Conversions
of anthracene to other products were 3.2% to sym -octahydroanthracene,
0.4% to asym -octahydroanthracene and 0.1% to alkylnaphthalenes. These
results indicate that $r_7 > r_5$ and $r_7 > r_6$. The reaction of dihydro-
anthracene under these conditions resulted in 5.2% conversion to tetra-
hydroanthracene. This result compared with 13% conversion of anthracene
to tetrahydroanthracene indicates that $r_2 > r_3$. Conversions of di-
hydroanthracene to other products were 1.6% to sym -octahydroanthracene,
0.5% to asym -octahydroanthracene and 0.6% to alkylnaphthalenes. A
small amount of isomerization of sym -octahydroanthracene to sym -
octahydrophenanthrene was also observed. These results indicate that
$r_3 > r_4$. Since the same amount of asym.-octahydroanthracene was
observed in reactions of anthracene and dihydroanthracene, it may be
concluded that most of the asym -octahydroanthracene is produced
through reaction step 5, or that $r_5 > r_4$. The conversion of dihydro-

anthracene to anthracene was 4.6%, indicating that $r_1 \gg r_{-1}$. Since sym -octahydroanthracene did not react under these reaction conditions (Table 3-17), it is concluded that $r_7 > r_8$, r_{11}.

The results of reactions of anthracene in the presence of $AlCl_3$ can also be explained by the reaction sequence given in Fig. 3-4. When the reactions were carried out at 225°C, and 800 psig for 0 and 1 hour, (Table 3-9), the conversion of anthracene to dihydroanthracene decreased with time while the conversions to tetrahydroanthracene, sym - and asym -octahydroanthracene, sym -octahydrophenanthrene, naphthalene, alkylnaphthalenes and tetralin increased. When the reaction of anthracene was carried out at 325°C and 1600 psig, (Table 3-22) small concentrations of partially hydrogenated anthracenes were obtained in the products, but higher amounts of unsaturated and partially saturated two ring compounds were obtained compared to the experiments in the presence of $ZnCl_2$. Alkyltetralins and sym -octahydrophenanthrene were also observed in the products. This indicates that reaction of sym - octahydroanthracene proceeds to form alkyltetralins and sym -octahydrophenanthrene. Due to the high reactivity of all the compounds in the presence of $AlCl_3$, the final products were mostly alkylbenzenes and tar. Similar results were obtained for reactions of dihydroanthracene and sym -octahydroanthracene.

The reaction sequence proposed for anthracene hydrogenation and cracking may be explained on the basis of carbonium ion intermediates. In the first step, anthracene is protonated. Protonation may occur at positions 1, 2 and 9. Position 9 is a much more likely site for protonation as indicated by the fact that log $(K_B)_9 = 3.5$, compared to log $(k_B)_1 = -3.4$ and log $(K_B)_2 = -4.9$ (68). (For definition of

log $(K_B)_i$, see section V-A). The high basicity of 9-position is the reason for the rapid rate of conversion of anthracene to dihydroanthracene, even in the presence of very weak acid catalysts.

$$(\text{II})$$
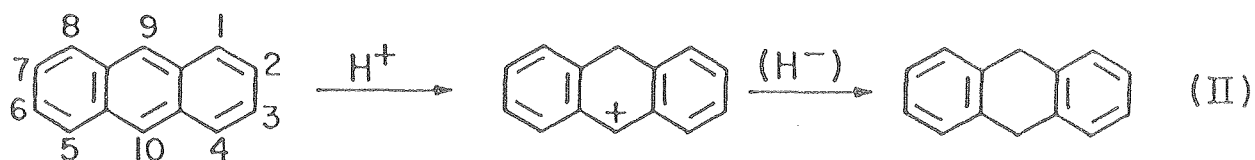
Protonation at the 1-position, followed by hydride abstraction and further hydrogenation results in formation of tetrahydroanthracene.

$$(\text{III})$$

Further hydrogenation of dihydroanthracene and tetrahydroanthracene results in the formation of sym -octahydroanthracene and asym -octahydroanthracene. Sym -octahydroanthracene may isomerize to form octahydrophenanthrene under proper reaction conditions by the following reactions.

$$(\text{IV})$$
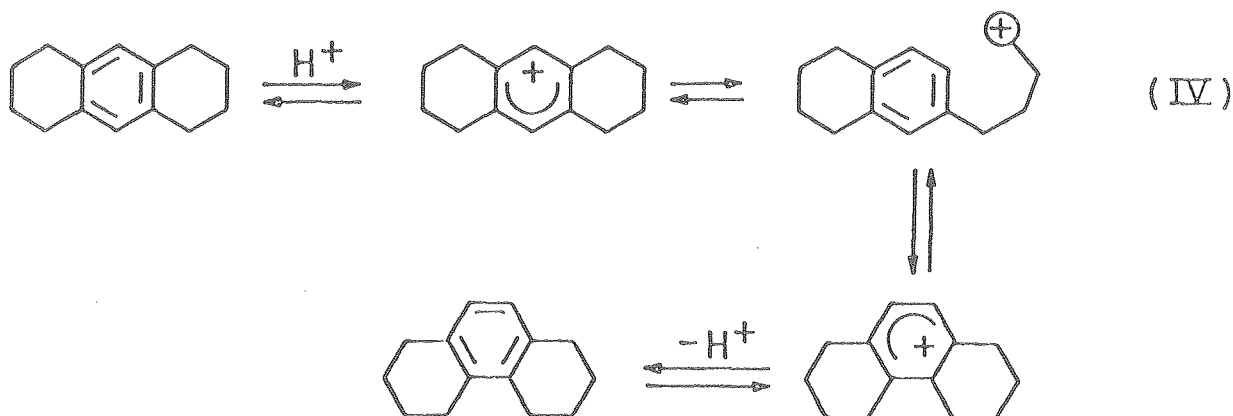
Reaction mechanisms can be envisioned for cracking the side rings of

sym -octahydroanthracene and tetrahydroanthracene and the central ring

of asym -octahydroanthracene which are similar to those proposed to

explain the cracking of tetralin.

E. Hydrogenation and Cracking of Phenanthrene

A possible reaction sequence for phenanthrene hydrogenation and

cracking, based on products observed in reactions of phenanthrene in the

presence of $ZnCl_2$ and $AlCl_3$ is presented in Fig. 3-5. A similar reaction

mechanism has been proposed for phenanthrene reaction, based on its

reactions at 400°C and 3400 psig in the presence of molten salt catalysts

by Nakatsuji, et al. (52). The above investigators have proposed that

cracking of the saturated side rings proceeds through an initial isomeri-

zation similar to that proposed for anthracene (see section D). These

authors did not indicate the possibility of hydrogenation of dihydro-
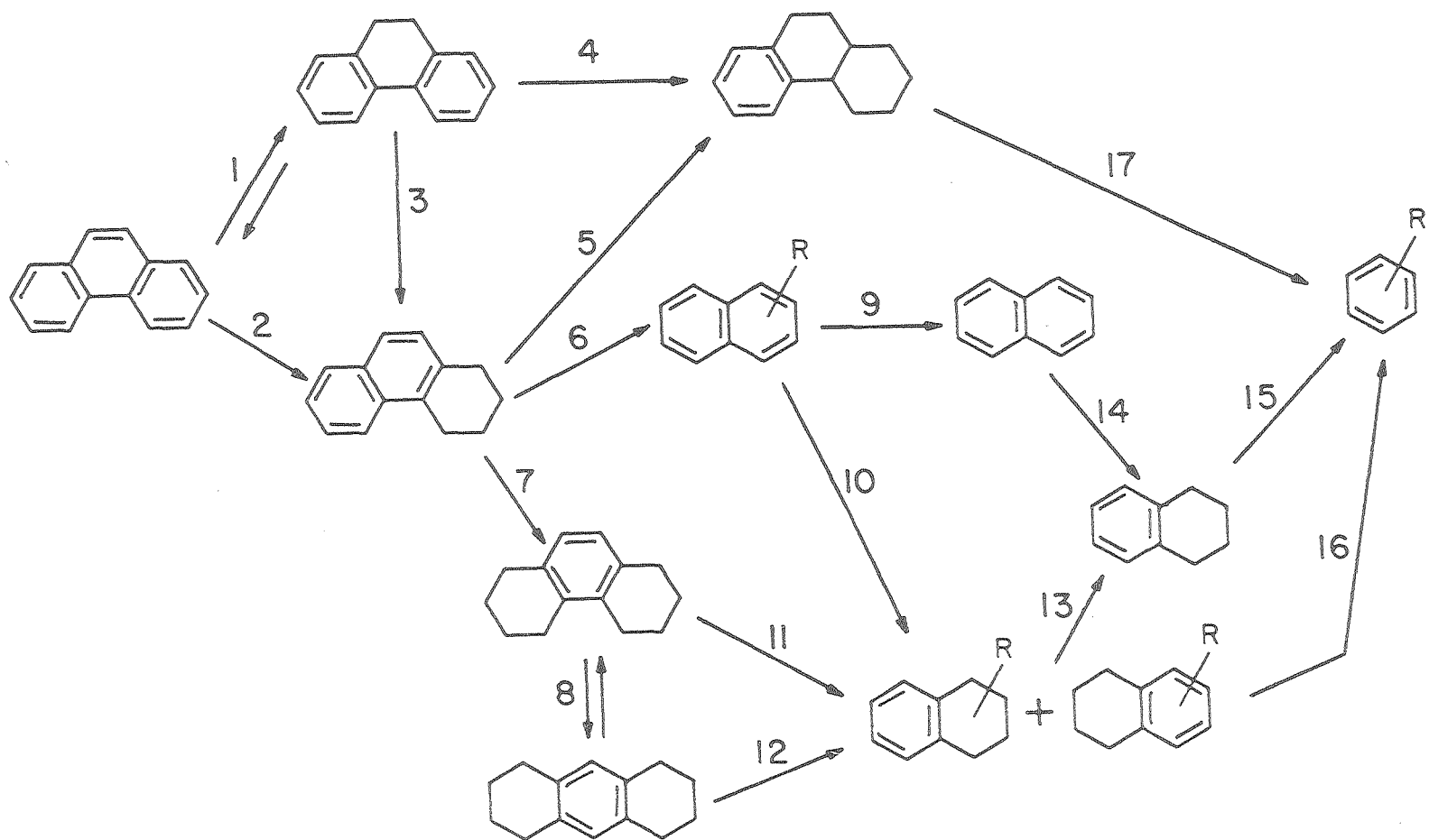
phenanthrene to tetrahydrophenanthrene, which was observed in the results

of the present work. They also proposed that cracking of the central

ring of dihydrophenanthrene occurs to give alkylbiphenyls. In the

present investigation, there was not enough evidence to confirm this

idea. The small amounts of biphenyl observed in reaction products of

phenanthrene and dihydrophenanthrene in the presence of $AlCl_3$ (Table 3-22)

could have resulted from coupling of two benzene molecules as well as

cracking of the central ring of phenanthrene. The reaction of phenan-

threne at 325°C and 1600 psig in the presence of $ZnCl_2$ was faster than

that of naphthalene, but much slower than that of anthracene, as indicated

by substrate conversions of 1.4%, 0.6% and 68% respectively (see Tables

3-16 and 3-17). This parallels the basicity of the above compounds.

Log K_B for phenanthrene is -3.5, compared to -4.0 for naphthalene and

Fig. 3-5. Hydrogenation and Cracking of Phenanthrene

XBL 803-8951

3.8 for anthracene (68). (See section A for definition of K_B.) Products observed in reactions of phenanthrene and dihydrophenanthrene were similar to those of anthracene and dihydroanthracene under the above reaction conditions. Conversions to products observed in the reactions of phenanthrene were 0.9% to dihydrophenanthrene, 0.2% to tetrahydrophenanthrene, 0.2% to sym -octahydrophenanthrene, 0.1% to asym -octahydrophenanthrene and 0.2% to naphthalene and alkylnaphthalenes. Conversions of dihydrophenanthrene to products under these reaction conditions were 0.3% to tetrahydrophenanthrene and 0.4% to sym -octahydrophenanthrene. The low conversions indicate that rates of the reactions via steps 1, 2, 3, etc., are low. There is not a noticeable difference between the relative reaction rates via these steps.

The proposed reaction sequence can be interpreted on the basis of carbonium ion intermediates. The initial protonation step of phenanthrene may occur at positions 1, 2, and 9 as is possible for anthracene. However, for phenanthrene, positions 1, 2 and 9 have about the same basicity (68). Thus, protonation at all these sites occurs with roughly equal probability. The products observed are dihydrophenanthrene and tetrahydrophenanthrene.

(I)
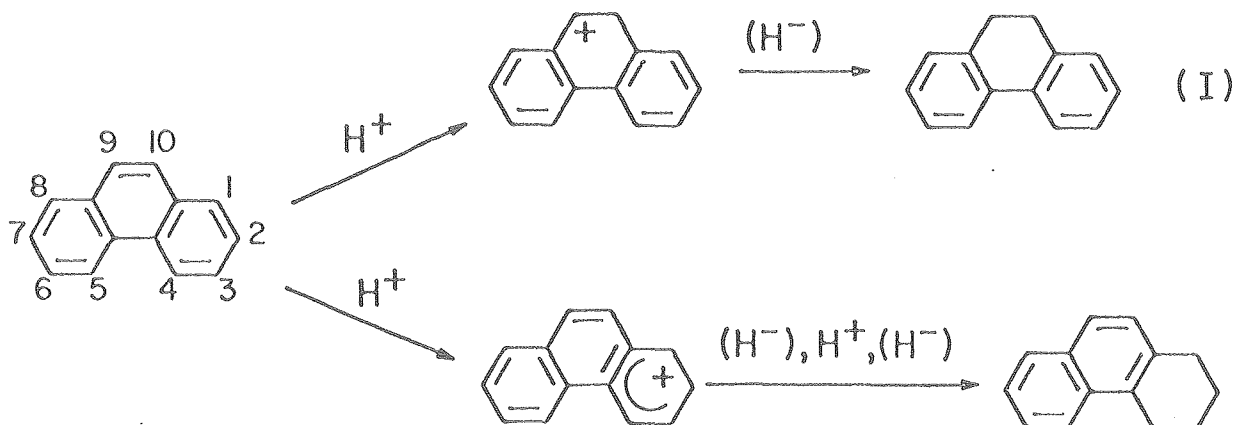
Further hydrogenation of dihydrophenanthrene and tetrahydrophenanthrene

result in formation of sym – and asym –octahydrophenanthrenes. Sym –

octahydrophenanthrene isomerizes to sym –octahydroanthracene (see

section D). Reaction paths for cracking the side rings of sym –octa–

hydrophenanthrene and tetrahydrophenanthrene are similar to the paths

proposed to explain the cracking of tetralin. Cracking of the central

ring of asym –octahydrophenanthrene occurs much more readily that that

of asym –octahydroanthracene because a secondary carbonium ion is formed

in the former case instead of a primary carbonium ion.

(II)
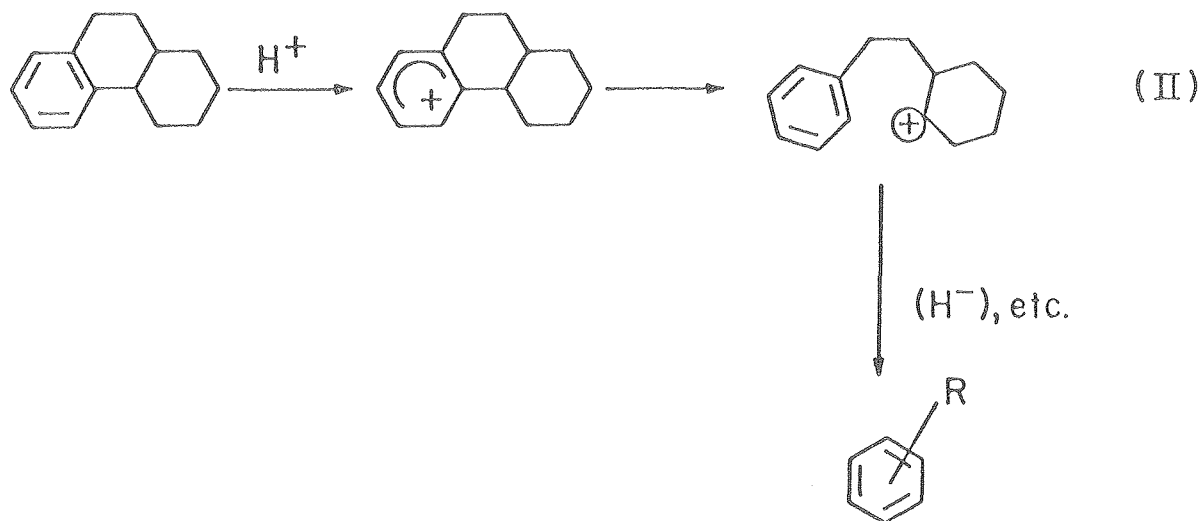
F. Hydrocracking of Fluorene

No reaction of fluorene was observed in the presence of $ZnCl_2$ at

325°C and 1600 psig (Table 3-17). However, when $AlCl_3$ was used, a

reaction occurred under the same reaction conditions (Table 3-22). A

possible reaction sequence for hydrocracking of fluorene, based on the

products observed during its reaction at 325°C and 1600 psig in the

presence of $AlCl_3$ is given in Fig. 3-6. This mechanism involves

cracking of the central ring at either the phenyl-phenyl bond (step 1),

or the phenyl-methyl bond (step 2), to form diphenylmethane and methyl–
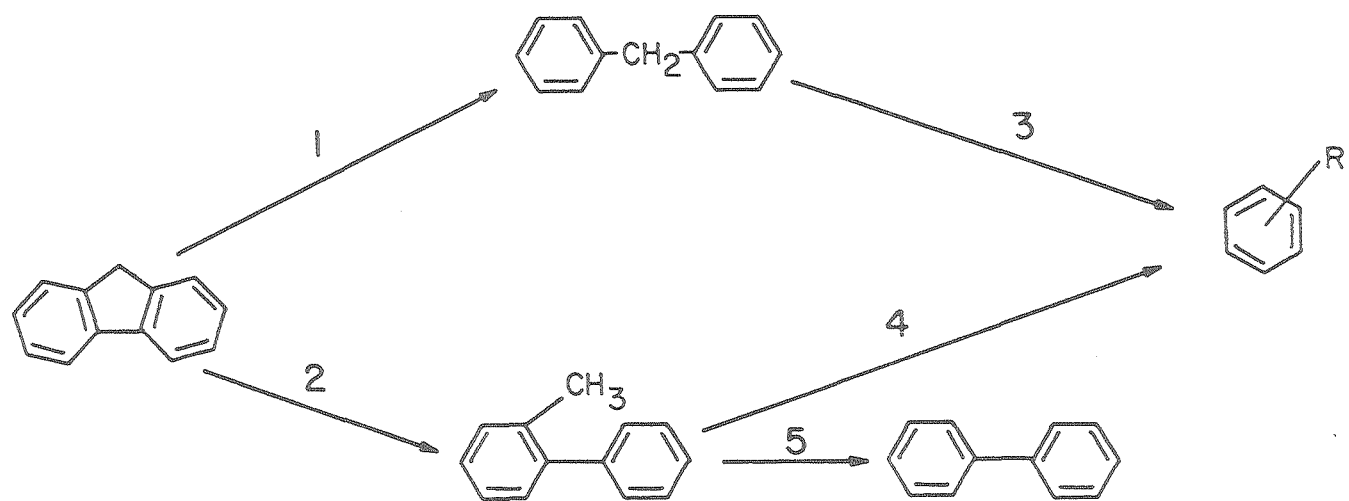
Fig. 3-6. Hydrocracking of Fluorene

XBL 803-8954

biphenyl. The above compounds in turn undergo cracking to form alkylbenzenes.

The total conversion of fluorene to products under the above reaction conditions in the presence of $AlCl_3$ was 97%, of which 78% was to tar and alkylbenzenes. Conversion to products which could be formed via step 2 and subsequent steps were 4.6% to methylbiphenyl, 6.6% to biphenyl and 1.8% to dimethylbiphenyl. It is difficult to make conclusive statements about the relative rates of reactions via the above steps because fluorene, diphenylmethane and methylbiphenyl are all reactive in the presence of $AlCl_3$. High rates of polymerization have been observed for fluorene, even at room temperature (43, 55) and for diphenylmethane under reaction conditions similar to those of the present work (82). The observed alkylbenzenes are produced mostly through cracking of diphenylmethane and methylbiphenyl. Biphenyl, which is formed as a result of disproportionation of methylbiphenyl, undergoes tar formation in preference to cracking under these reaction conditions (82).

The reaction sequence given in Fig. 3-6 can be interpreted in terms of carbonium ion mechanisms. In the first step of the reaction, one of the aromatic rings is protonated.

$$(I)$$
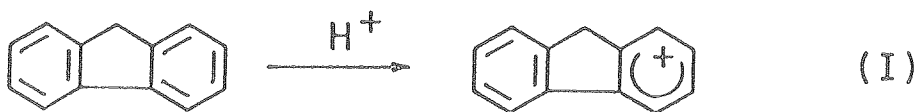
The resulting carbonium ion can readily add to another molecule to form bifluorene and higher polymers (55), or undergo cleavage of the central ring. Cracking can occur at the phenyl-phenyl bond, because the resulting carbonium ion can be resonance stabilized.
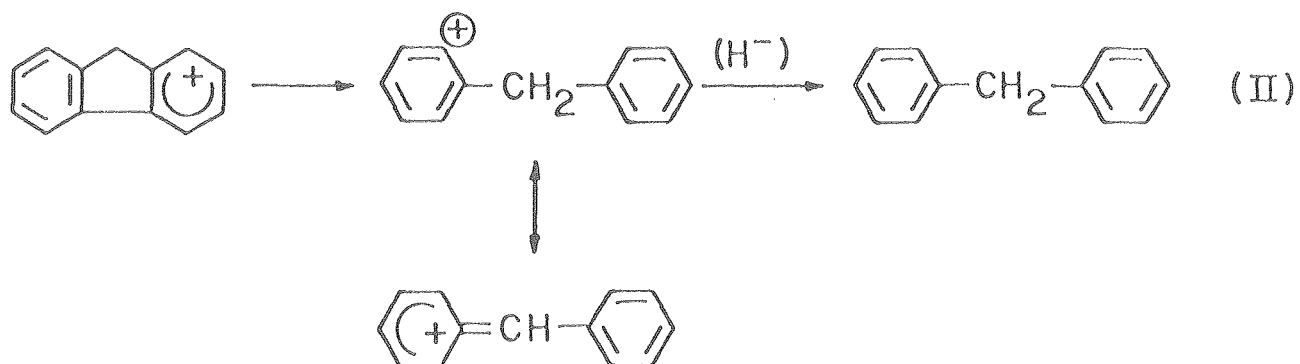
Cracking at the phenyl-methyl bond results in formation of a primary

carbonium ion which is resonance stabilized in the manner shown below:
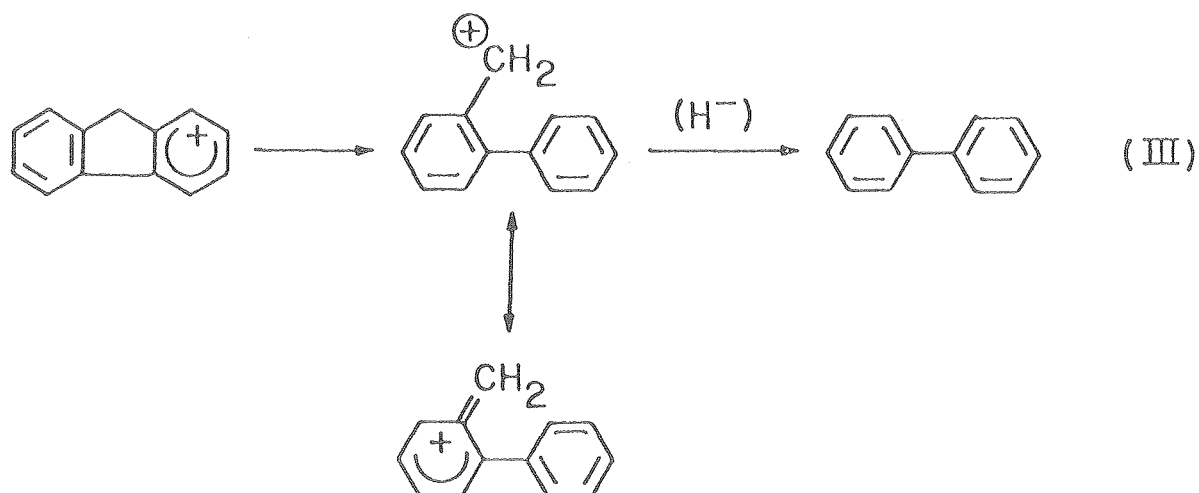
Cracking of diphenylmethane may occur by the following pathway (82).
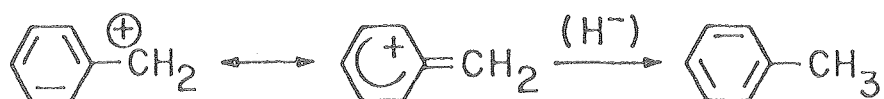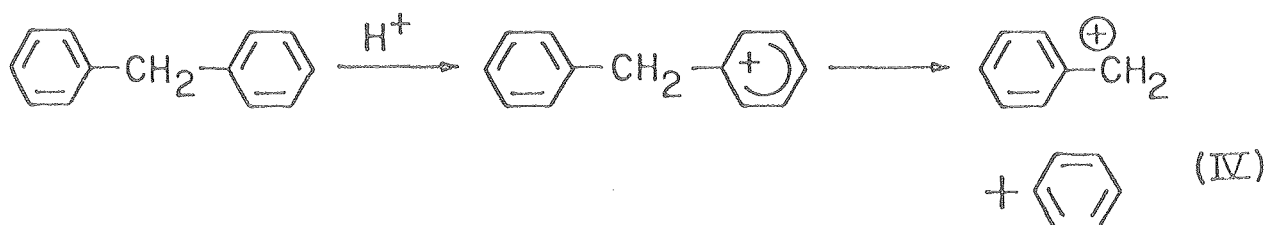
And cracking and disproportionation of methylbiphenyl may occur by the
following pathways.

$$(\text{V})$$
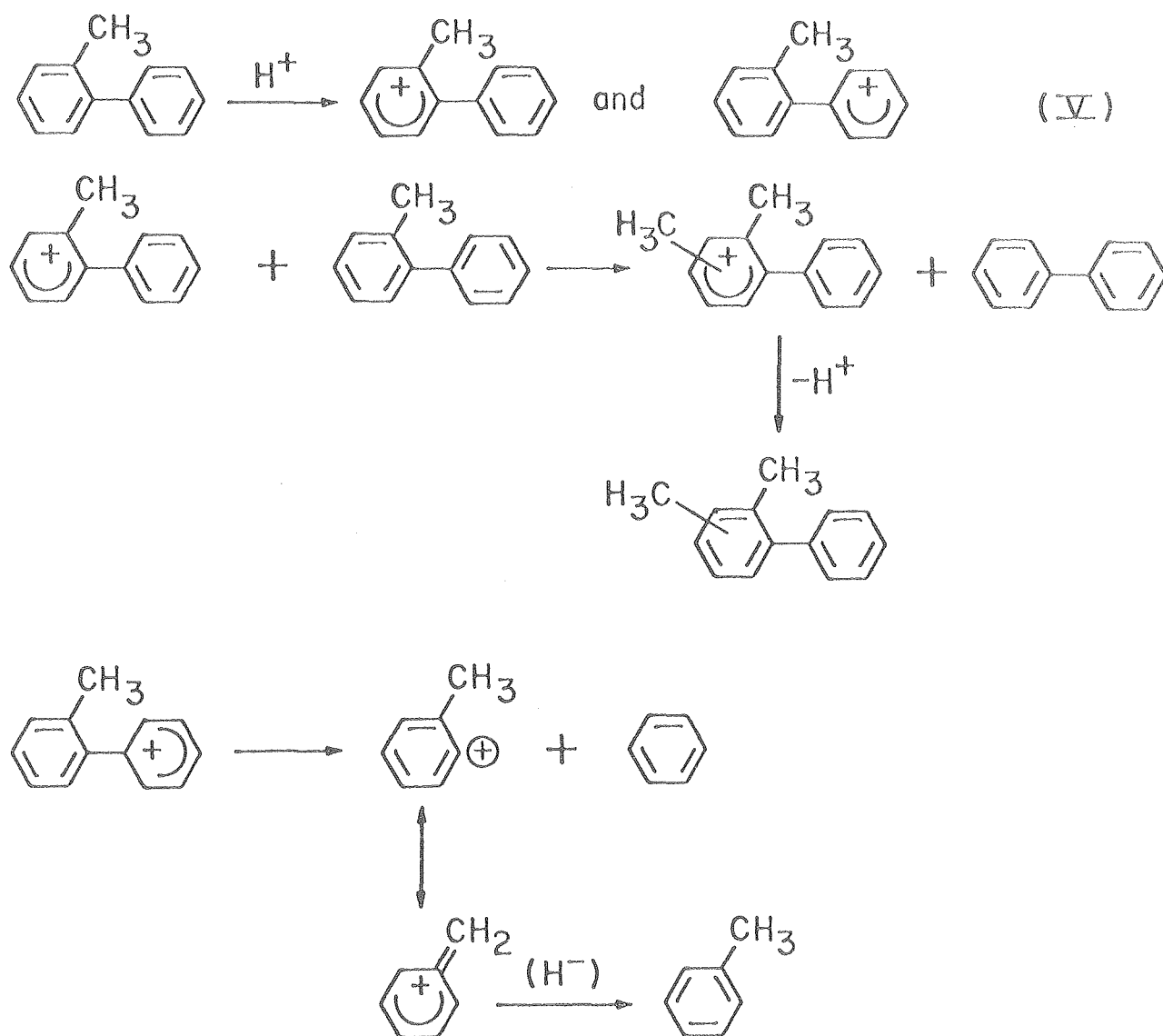
All the carbonium ion intermediates in the above mechanisms can react
with other molecules in Scholl type condensation reactions to form tar
(82,83).

G. Hydrocracking of 9,10-Dihydro-5H-dibenzo[a,d]cycloheptene

A possible reaction sequence for the hydrocracking of dihyrodibenzo-
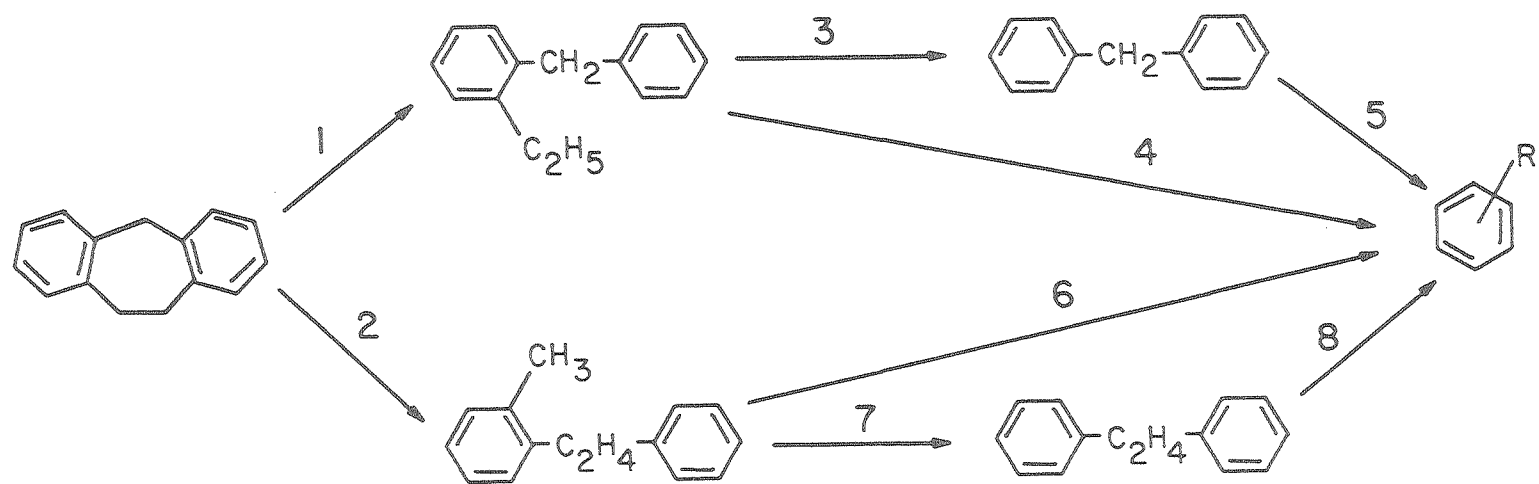
Fig. 3-7. Hydrocracking of Dihydrodibenzocycloheptene

cycloheptene based on products observed in its reactions in the presence of $ZnCl_2$ and $AlCl_3$ is presented in Fig. 3-7. This sequence involves cracking of the central ring at the ethyl-phenyl bond (step 1), or the methyl-phenyl bond (step 2). The resulting alkyldiphenylalkanes undergo disproportionation and cracking to form alkylbenzenes, or undergo tar formation.

Reaction of dihydrodibenzocycloheptene at 325°C and 1600 psig in the presence of $ZnCl_2$ (Table 3-17), gave conversions of 0.7% to ethyl-diphenylmethane (through step 1), and 2.2% to methylbibenzyl (through step 2). Small amounts of diphenylmethane and bibenzyl were also observed. These results indicate that reaction via step 2 is somewhat faster than via step 1, or that $r_2 > r_1$. Reaction of the above compound under similar conditions in the presence of $AlCl_3$ (Table 3-22), resulted in conversions of 7.8% to ethyldiphenylmethane, 1.7% to methylbibenzyl, 0.3% to diphenylmethane and 17.5% to bibenzyl. Substantial amounts of tar and alkylbenzenes were also observed. These results again indicate that reaction via step 2 is more favored than via step 1.

The reaction sequence shown in Fig. 3-1 can be explained based on carbonium ion intermediates. The carbonium ion intermediate produced in the cracking of the methyl-phenyl bond to form methylbibenzyl is resonance stabilized in the manner shown below.
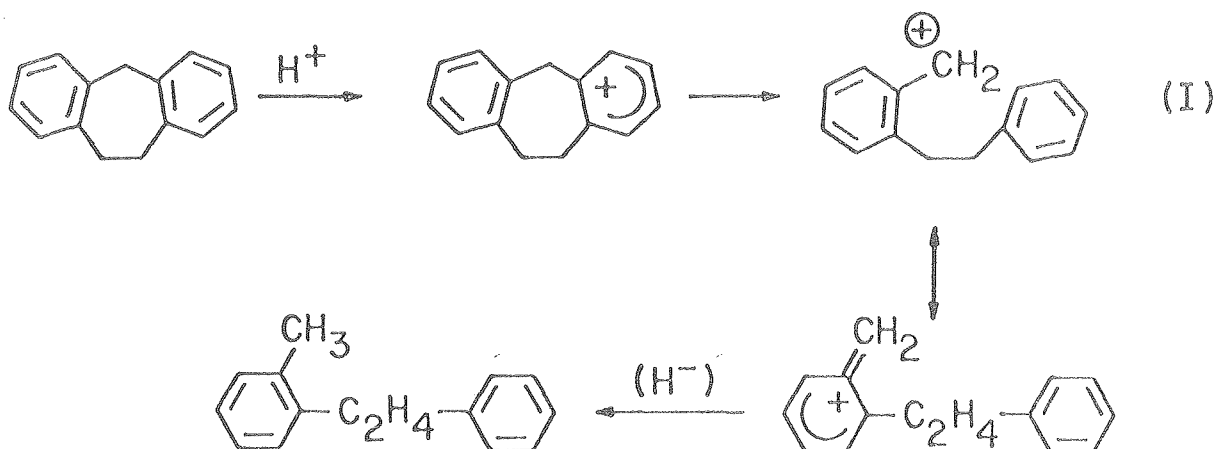
The carbonium ion intermediate formed in the cracking of the ethyl-
phenyl bond to form ethyldiphenylmethane is also resonance stabilized:

(II)

(H⁻)
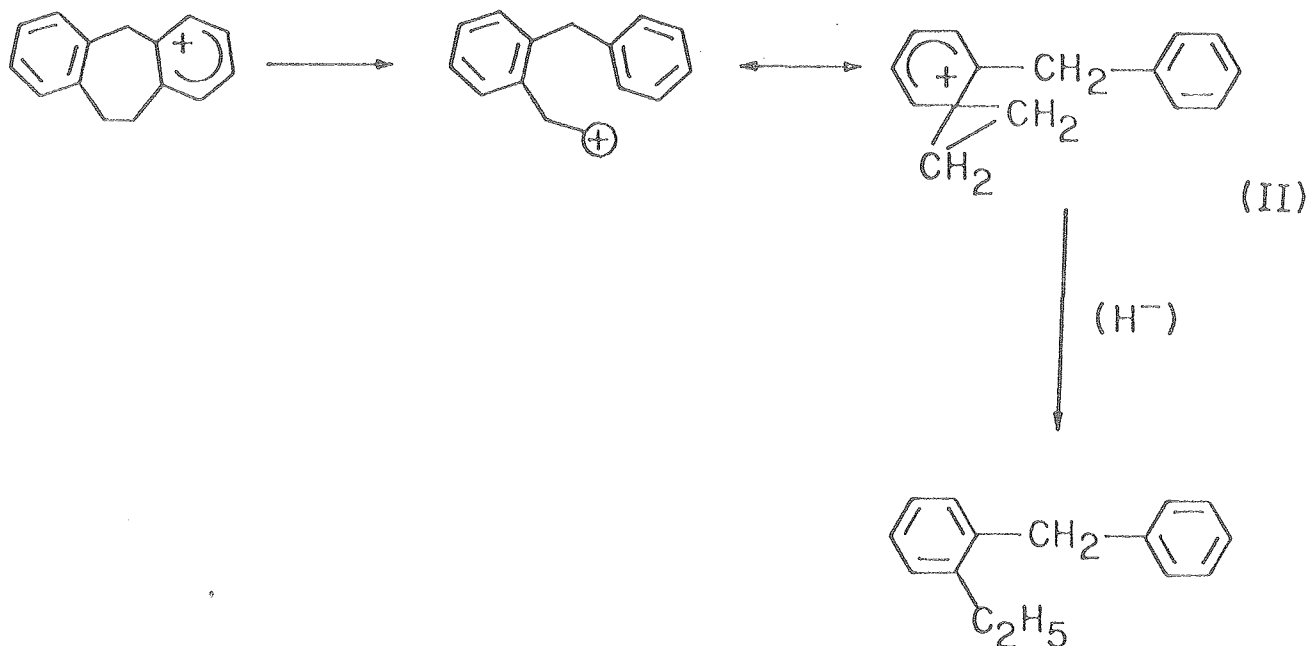
However, there is a large degree of strain in this case (81). As a
result, the carbonium ion formed via reaction path 1 is more stable
than that formed via react ion path 11. This explains why reaction
along step 2 (Fig. 3-7) is favored over reaction along step 1.

The other steps in the reaction sequence (Fig. 3-7) involve dis-
proportionation and cracking of alkyldiphenylalkanes and cracking of
diphenylalkanes. These steps are similar to those of the reaction of
fluorene, discussed in section F.

CHAPTER 4:   CONCLUSIONS

This work has provided information on the hydrogenation and cracking of selected two and three fused-ring aromatic compounds in the presence of $ZnCl_2$ and $AlCl_3$. Substrate structures were selected to resemble those found in coal. Information was obtained regarding relative reactivity of structures based on number of rings, orientation of rings and substituents present on rings. Reaction mechanisms were proposed to explain the products formed and the trends in substrate reactivity with structure.

In the presence of the weaker catalyst, $ZnCl_2$, using dilute solutions of each substrate in cyclohexane, reaction temperature of 325°C, reaction pressure of 1600 psig under hydrogen atmosphere, substantial reactivity differences were observed amongst the compounds. Anthracene was found to be much more reactive than phenanthrene, which was in turn more reactive than naphthalene. There was a correlation between basicity of these compounds and the observed relative reactivities. For three ring compounds containing a saturated central ring, cracking of the central ring was observed when the ring had seven carbons. No cracking of the central ring was observed when the ring had five or six carbons. The presence of a hydroxyl group on 1-position of a ring in naphthalene increased the reactivity of this ring towards hydrogenation to a great extent. The reactivity of the neighboring ring was also enhanced, but to a much lesser extent. The presence of a methyl group on 1-position on a ring increased the reactivity of this ring and the neighboring ring equally. The effect was not as pronounced as that of the hydroxyl group.

All substrates were quite reactive in the presence of the stronger catalyst, $AlCl_3$, and under reaction conditions identical to the experiments with $ZnCl_2$. This resulted in substantial tar formation as well as high conversions to liquid products. Hydrogenation and cracking of the rings were observed. The order of reactivity for simple fused ring clusters was again anthracene > phenanthrene > naphthalene, but the differences between the reactivities were not as pronounced as those observed with $ZnCl_2$. The cracking of the central ring occurred for both five and seven carbon rings. The reactivity of the structures towards cracking was again higher for the seven carbon ring. Enhancement of reactivity of naphthalene type structures was again observed when methyl or hydroxyl substituents were present.

The source of hydrogen used in hydrogenation and cracking of substrates was found to depend on the nature of the catalyst. In the presence of $ZnCl_2$, gaseous hydrogen was the major source of hydrogen. In the presence of the stronger acid catalyst, $AlCl_3$, the reaction medium provided most of the hydrogen for hydrogenation and cracking reactions. A possible source of hydrogen in this case could have been Scholl condensation of substrates or reaction intermediates, as evidenced by the high amount of tar observed in the products.

Reaction mechanisms were proposed for hydrogenation and cracking of substrates based on products observed in reactions of substrates as well as reactions of products of partially hydrogenated intermediates of substrates. These mechanisms were based on carbonium ion intermediates.

Naphthalene hydrogenation proceeds through a slow step to form dihydronaphthalene, followed by a rapid step to form tetralin. Cracking

of tetralin to form alkylbenzenes or further hydrogenation to form
decalin are both relatively slow, the former having the more preferred
path. The presence of the electron donor methyl substituent group in
1-methylnaphthalene increases the rate of hydrogenation and cracking of
the two-ring cluster. This is due to the better resonance stabilization
of the carbonium ion intermediates. The hydroxyl group in 1-naphthol is
a strong activating substituent for electrophilic reactions. Thus, 1-
naphthol hydrogenates rapidly, through 1-tetralone intermediate, to form
1,2,3,4-tetrahydro-1-naphthol. This is followed by rapid deoxylation-
hydrogenation or deoxylation-dehydrogenation resulting in tetralin and
naphthalene as final products. Hydrogenation of 1-naphthol to 5,6,7,8-
tetrahydro-1-naphthol is slower than the above path but more rapid than
that of naphthalene. The presence of the hydroxyl group on the un-
saturated ring increases the rate of cracking of the saturated ring
compared to tetralin, again because the intermediate carbonium ion has
better resonance stabilization.

Anthracene reacts through a sequence of hydrogenation, isomeriza-
tion and cracking to form alkylnaphthalenes and alkyltetralins. Hydroge-
nation to form dihydro and tetrahydro derivatives is very rapid.
Hydrogenation to octahydroanthracene occurs at a high rate, but slower
than the above steps. Both symmetric and asymmetric octahydroanthracenes
are formed. Symmetric octahydroanthracene isomerizes to form symmetric
octahydrophenanthrene. The following steps are cracking of the saturated
side rings of tetrahydro and octahydro derivatives to form alkyl-
naphthalenes and alkyltetralins. These steps are slower than
hydrogenation steps. Cracking of the central ring also occurs. The
rate of this step is negligible compared to the above sequence.

Phenanthrene reaction paths are similar to those of anthracene, but the rate of hydrogenation is slower.

Cracking of the five carbon central ring in fluorene occurs by cleavage of either the phenyl-phenyl or the phenyl-methyl bonds. The latter occurs more readily because the intermediate carbonium ion has better resonance stabilization. Cracking of the seven carbon central ring of dihydrodibenzocycloheptene occurs at both phenyl-ethyl and phenyl-methyl bonds. Both these steps are more rapid than the reaction steps in fluorene. Again, cleavage at the phenyl-methyl bond occurs more rapidly, since the intermediate carbonium ion has better resonance stabilization.

REFERENCES

1. Walter, K., Feldmann, H. F., Hiteshue, R. W., Preprints, Div. of Fuel Chem., Amer. Chem. Soc., 14(4), 19 (1970).

2. Low, J. Y., Ross, D. S., Preprints, Div. of Fuel Chem., Amer. Chem. Soc., 22(7), 118 (1977).

3. Hiteshue, R. W., Kawa, W., U. S. Patent 3,556,978 (January 19, 1971).

4. Hodek, W., Kolling, C., Fuel, 52, 220 (1973).

5. Schlosberg, R. H., Wright, F. J., Hartgernik, R. L., U. S. Patent 4,072,475 (February 7, 1978).

6. Kurokawa, M., Hirota, W., Takeya, G. Takeya, G., Takenaka, Y., J. Soc. Chem. Ind. Japan, 44, 776 (1941).

7. Zielke, C. W., Struck, R. T., Evans, J. M., Costanza, C. P., Gorin, E., Ind. Eng. Chem., Proc. Des. Dev., 5(2), 158 (1966).

8. Struck, R. T., Clark, W. E., Dudt, P. J., Rosenhoover, W. A., Zielke, C. W., Gorin, E., Ind. Eng. Chem., Proc. Des. Dev. 8(4), 546 (1969).

9. Zielke, C. W., Rosenhoover, W. A., Gorin, E., Adv. Chem. Ser., 151, 153 (1976).

10. Consolidation Coal Co., Library, PA, Research Div., Contract no. D1-14-01-0001-310 (1968-1972).

11. Scarrah, W. P., Hydrocracking of Montana Coals Through the Use of Massive Quantities of Molten Salt Catalysts, Ph.D. Thesis, Department of Chemical Engineering, Montana State University, Bozeman, MN (1973).

12. Bodily, D. M., Lee, H. D., Hill, G. R., Preprints, Div. of Fuel Chem., Amer. Chem. Soc., 16(2), 124 (172).

13. Wood, R. E., Wiser, W. H., Ind. Eng. Chem., Proc. Des. Dev., 15(1), 144 (1976).

14. Tanner, K. I., Bell, A. T., Catalytic Conversion of Solvent Refined Coal to Liquid Products, Lawrence Berkeley Laboratory Report No. 6807, Berkeley, CA (1978).

15. Holten, R. R., Vermeulen, T., Hydrogenolysis of a Subbituminous Coal with Molten Zinc Chloride Solutions, Lawrence Berkeley Laboratory Report No. 5948, Berkeley, CA (1977).

16. Shinn, J. H., Vermeulen, T., Coal Conversion Catalysis Using Zinc Chloride in Organic Media, Lawrence Berkeley Laboratory Report No. 9372, Berkeley, CA (1979).

17. Given, P. H., Fuel, 39, 147 (1960).

18. Wiser, W. H., Proceedings of the Electric Power Institute, Conference on "Coal Catalysis", p. 3-53 to 3-96, Palo Alto, CA (September 1973).

19. Wiser, W. H., "Some Chemical Aspects of the Conversion of Coal to Liquid and Gaseous Fuels", Proceedings, Research in Coal Technology, OCR/NSF/RANN Workshop, p, 3-53, Buffalo, NY (October 1974).

20. Hill, G. R., Lyon, L. B., Ind. Eng. Chem., 54(6), 37 (1962).

21. Ghosh, G., Banerjee, A., Mazumdar, B. K., Fuel, 54, 294 (1975).

22. Huston, J. L., Scott, R. G., Studier, M. H., Fuel, 55, 281 (1976).

23. Whitehurst, D. D., Farcasiu, M., Mitchell, T. O., Dicker, J. J., Jr., The Nature and Origin of Asphaltenes in Processed Coal, EPRI Report AF-480, Prepared by Mobil Research & Development Corporation, Princeton, NJ (July 1977).

24. Benjamin, B. M., Raaen, V. F., Maupin, P. H., Brown, L. L., Collins, C. J., Fuel, 57, 269 (1978).

25. Brown, J. K., Ladner, W. R., Sheppard, N., Fuel, 39, 79, 87 (1960).

26. Hayatsu, R., Winans, R. E., Scott, R. G., Moore, L. P., Studier, M. H., Preprints, Div. of Fuel Chem., Amer. Chem. Soc., 22(5), 156 (1977).

27. Chakrabartty, S. K., Berkowitz, N., Preprints, Div. of Fuel Chem., Amer. Chem. Soc., 22(5), 107 (1977).

28. Pines, A., Wemmer, D. E., Stanford Research Institute, Coal Chemistry Workshop, I., Session IV, Paper 18, Menlo Park, CA (1976).

29. Whitehurst, D. D., Properties and Liquefaction Behavior of Western Coals in Synthetic Recycle Solvents, Presented at EPRI Contractors Conference, Palo Alto, CA (May 1979).

30. Mazumdar, B. K., Chakrabartty, S. K., Lahiri, A., Fuel, 41, 129 (1962).

31. Lowry, H. H., ed., Chemistry of Coal Utilization-Supplementary Volume, John Wiley & Sons, NY (1963).

32. Hayatsu, R., Winans, R. E., Scott, R. G., Moore, L. P., Studier, M. H., Fuel, 57, 541 (1978).

33. Speight, J. G., _Appl. Spec. Rev._, _5_, 211 (1972).

34. Deno, N. C., _Tet. Let._, _20_, 1703 (1977).

35. Deno, N. C., Greigger, B. A., Stroud, S. G., _Fuel_, _57_, 455 (1978).

36. Mazumdar, B. K., Ganugly, S., Sanyal, P. K., Lahiri, A., _Adv. Chem. Ser._, _55_, 475 (1966).

37. Blom, L., Edelhausen, L. E., Van Krevelen, D. W., _Fuel_, _36_, 135 (1957).

38. Vaughan, G. A., Swithenbank, J. J., _Analyst_, _95_, 890 (1970).

39. Kling, A., Florentin, D., _Compt. Rend._, _182_, 526 (1926).

40. Kling, A., Florentin, D., _Compt. Rend._, _184_, 822 (1927).

41. Winter, H., Free, G., _Brennstoff. Chem._, _12_, 451 (1931).

42. Schmerling, L., Ipatieff, V. N., _U. S. Patent 2,388,937_ (November 13, 1945).

43. Prey, V., Schindlbauer, H., Cmelka, D., _Angew. Makromol. Chem._, _28_, 137 (1973).

44. Siskin, M., Wristers, J. P., _U. S. Patent 3,888,937_ (June 10, 1975).

45. Blom, P. W. E., Dekker, J., Fourie, L., Kruger, J. A., Potgleter, H. G. J., _J. S. Afr. Chem. Inst._, _28_(1), 130 (1975).

46. Morita, M., Hirosawa, K., _J. Fuel Soc. Jpn._, _54_, 580, 677 (1975).

47. Morita, M., Horosawa, K., _Nippon Kagaku Kaishi_, No. 9, 1555 (1975).

48. Kikkawa, S., Nomura, M., Murase, K., _Asahi Garasu Kogyo Gijustu Shoreikai Kenkyu Hokoku_, _28_, 259 (1976).

49. Kikkawa, S., Nomura, M., Kubo, T., Nakatsuji, Y., _Chem. Lett._, _12_, 1383 (1976).

50. Kikkawa, S., Nomua, M., Murase, K., _Sekiyu Gakkai Shi_, _19_(10), 863 (1976).

51. Morita, M., Hirosawa, K., _Nippon Kagaku Kaishi_, No. 8, 1259 (1976).

52. Nakatsuji, Y., Kubo, T., Nomura, M., Kikkawa, S., _Bull. Chem. Soc. Jpn._, _51_(2), 618 (1978).

53. Nakatsuji, Y., Ikkaku, Y., Nomura, M., Kikkawa, S., _Bull. Chem. Soc. Jpn._, _51_(12), 3631 (1978).

54. Poutsma, M. L., Dworkin, A. S., Brynestad, J., Brown, L. L., Benjamin, B. M., Smith, G. P., Tet. Lett., 10, 873 (1978).

55. Wen, L. S., Kovacic, P., Tetrahedron, 34(18), 3723 (1978).

56. Olah, G. A., Friedel-Crafts Chemistry, John Wiley & Sons, NY (1973), p. 12.

57. Ibid., p. 64.

58. Nenitzescu, C. D., Cantuniari, I. P., Chem. Ber., 66, 1097 (1933).

59. Ipatieff, V. N., Komarewsky, V. I., J. Am. Chem. Soc., 56, 1926, (1934).

60. Pines, H., Abraham, B. M., Ipatieff, V. N., J. Am. Chem. Soc., 70, 1742 (1948).

61. Nenitzescu, C. D., in Carbonium Ions, ed., Olah, G. A., Schleyer, P.V.R., Wiley-Interscience, NY (1970), Vol. I., p. 463.

62. Wilson, T. P., Caflisch, E. G., Hurley, G. F., J. Phys. Chem., 62, 1059 (1958).

63. Frye, C. G., J. Chem. Eng. Data, 7(4), 592 (1962).

64. Frye, C. G., Weitkamp, A. W., J. Chem. Eng. Data, 14(3), 372 (1969).

65. Olah, G. A., Friedel-Crafts Chemistry, John Wiley & Sons, NY (1973), p. 224.

66. Ibid., p. 321.

67. Ibid., p. 217.

68. Brouwer, D. M., Mackor, E. L., McLean, C., in Carbonium Ions, ed., Olah, G. A., Schleyer, P. V. R., Wiley-Interscience, NY (1970), Vol. II, p. 837.

69. Gold, V., Tye, F. L., J. Chem. Soc., 2172 (1952).

70. Dallinga, G., Mackor, E. L., Verrijan Stuart, A. A., Mol. Phys., 1 123 (1958).

71. McLean, C., Van Der Waals, J. M., Mackor, E. L., Mol. Phys., 1, 123 (1958).

72. Olah, G. A., Staral, J. S., Asencio, G., Liang, G., Forsyth, D. A., Mateescu, G. D., J. Am. Chem. Soc., 100(20), 6299 (1978).

73. Olah, G. A., Schlosberg, R. H., Porter, R. D., Mo, Y. K., Kellye, D. P., Mateescu, G. D., J. Am. Chem. Soc., 94, 2034 (1972).

74. Qader, S. A., J. Ins. Petrol., 59, 178 (1973).

75. Wristers, J., J. Am. Chem. Soc., 99(15), 5051 (1977).

76. Larsen, J. W., Chang, L. W., J. Org. Chem., 44(7), 1168 (1979).

77. Stock, L. M., Aromatic Substitution Reactions, Prentice Hall, Inc., NY, (1968), p. 74.

78. Streitwieser, Jr., A., Heathcock, C. H., Introduction to Organic Chemistry, Macmillan Publishing Co., Inc., NY (1976), p. 1047.

79. Balaban, A. T., Bebtzescym. C. D., in Friedel-Crafts and Related Reactions, ed., Olah, G. A., Interscience Publishers, NY (1964), Vol. II, part 2, p. 979.

80. Wristers, J. W., J. Am. Chem. Soc., 97(15), 4312 (1975).

81. Personal communications with Prof. P. K. Vollhardt, Department of Chemistry, University of California, Berkeley, California.

82. Taylor, N. D., Bell, A. T., The Chemistry of Coal Model Compounds: Cleavage of Aliphatic Bridges Between Aromatic Nuclei Catalyzed by Lewis Acids, Lawrence Berkeley Laboratory Report No. 7807, Berkeley, CA (1979).

83. Conklin, K. M., Bell, A. T., Hydrogenation, Cracking and Hydrogenolysis of Bibenzyl in a High-Pressure Stirred Autoclave, Lawrence Berkeley Laboratory Report No. 4440, Berkeley, CA (1975).